

Standardisation of chamber technique for CO₂, N₂O and CH₄ fluxes measurements from terrestrial ecosystems

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Abstract. Chamber measurements of trace gas fluxes between the land surface and the atmosphere have been conducted for almost a century. Different chamber techniques, including static and dynamic, have been used with varying degrees of success in estimating greenhouse gases (CO_2 , CH_4 , N_2O) fluxes. However, all of these have certain disadvantages which have either prevented them from providing an adequate estimate of greenhouse gas exchange or restricted them to be used under limited conditions. Generally, chamber methods are relatively low in cost and simple to operate. In combination with the appropriate sample allocations, chamber methods are adaptable for a wide variety of studies from local to global spatial scales, and they are particularly well suited for in situ and laboratory-based studies. Consequently, chamber measurements will play an important role in the portfolio of the Pan-European long-term research infrastructure Integrated Carbon Observation System. The respective working group of the Integrated Carbon Observation System Ecosystem Monitoring Station Assembly has decided to ascertain standards and quality checks for automated and manual chamber systems instead of defining one or several standard systems provided by commercial manufacturers in order to define minimum requirements for chamber measurements. The defined requirements and recommendations related to chamber measurements are described here.

Keywords: ICOS, protocol, greenhouse gas, ecosystem, automated chamber system, manual chamber system

INTRODUCTION

Chamber measurements of trace gas fluxes between the land surface and the atmosphere have been conducted for almost a century (Lundegårdh, 1927, 1928). Henrik Lundegårdh is commonly named as the first scientist who measured soil respiration in the field. He already used a chamber placed on a collar that had been inserted into the soil beforehand. For decades, until the eddy covariance (EC) technique has become the standard technique to estimate net carbon dioxide (CO_2) exchange (Aubinet *et al.*, 2012), chamber measurements have been the prevailing technique to monitor the CO_2 exchange between the atmosphere and soil, plant organs or complete ecosystems (Livingston and Hutchinson, 1995; Pumpanen *et al.*, 2004; Wohlfahrt *et al.*, 2005; Acosta *et al.*, 2013). In the case of methane (CH_4) and nitrous oxide (N_2O), for which fast and precise analysers have only been developed very recently and are more expensive than fast CO_2 sensors, chambers still provide the majority of information and are the most commonly used flux measurement method (Denmead, 2008).

CO_2 , CH_4 and N_2O are the three greenhouse gases (GHGs) which are most commonly monitored using the chamber method. CO_2 is one of the most common and important trace gases in the earth-ocean-atmosphere system. It has both natural and anthropogenic sources. Within the natural carbon cycle, CO_2 plays a key role in a number of biological processes (photosynthesis, respiration *etc.*). Coal, oil, natural gas, and wood mostly consist of carbon, so combustion of these fuels releases CO_2 into the atmosphere, and this together with land use change processes, has been the cause of the continuous increase in atmospheric

CO_2 abundance over the last several decades. Carbon dioxide abundances are reported in dry-air mole fraction, $\mu\text{mol mol}^{-1}$, (parts-per-million, 10^{-6} , usually abbreviated ppm). CO_2 concentrations in the atmosphere increased by 40 % from 278 ppm in 1750 to 406 ppm in 2017, (NOAA/ESRL, 2017).

CH_4 is acting as a strong greenhouse gas, and it plays important roles in determining the oxidizing capacity of the troposphere and in stratospheric ozone depletion. It has both natural and anthropogenic sources. There are still many regions with strong CH_4 sources that are poorly characterized, including populated regions of the mid latitudes of the northern hemisphere, agricultural regions in South and Southeast Asia and the tropics in general, and vast regions of the Russian Arctic, where natural wetlands and fossil fuel exploitation result in significant emissions. Methane abundances are reported as CH_4 in dry-air mole fraction, (parts-per-billion, 10^{-9} , usually abbreviated ppb). During the same time interval as CO_2 , CH_4 increased by 150 % from 722 ppb in 1750 to 1859 ppb in 2017, (NOAA/ESRL, 2017)

N_2O has both natural and anthropogenic sources. Sources include soils under natural vegetation, agriculture, oceans, fossil fuel combustion and biomass and biofuel burning. Nitrous oxide is inert in the troposphere. Its major sink is through photochemical transformations in the stratosphere that decreases the abundance of stratospheric ozone. The units of N_2O measurements are dry-air mole fraction (ppb). N_2O increased by 20% from 271 ppb in 1750 to 329 ppb in 2017, (NOAA/ESRL, 2017).

The concentration of the three greenhouse gases CO_2 , CH_4 and N_2O have increased in the atmosphere since pre-industrial times due to anthropogenic emissions from the use of fossil fuel as a source of energy and from land use and land use change, in particular agriculture. The observed changes in the atmospheric concentration of CO_2 , CH_4 and N_2O result from the dynamic balance between anthropogenic emissions, and the perturbation of natural processes that lead to a partial removal of these gases from the atmosphere (IPCC, 2013).

Chamber measurements are relatively simple to operate and adaptable to a wide variety of studies, and they are important tools in situations where the EC technique cannot be applied. Furthermore, they are useful to determine the spatial heterogeneity of fluxes of GHGs, to partition the net fluxes of CO_2 into their components (respiration and gross primary production), as well as to offer supporting data for the gap-filling of the EC data. Even though the manual chamber measurements allow users to investigate the inter-annual variations of soil GHGs and the influence of environmental factors on them during the growing season, they may not be consistent throughout the year and may miss specific weather events; such as wet or dry conditions. Automated chambers have the great advantage of being able to measure continuously for long periods, regardless of

the weather and time of day. The use of automated systems for GHG efflux allows accurate measurements, minimal disturbance of the soil surface, and high resolution datasets for extended periods of time (*e.g.* Korkiakoski *et al.*, 2017). Due to their advantages, chamber measurements will play an important role in the portfolio of the Pan-European long-term research infrastructure ICOS. However, a universal chamber system (commercial or homemade) does not exist. The respective working group of the ICOS Ecosystem Monitoring Station Assembly (MSA) has decided to ascertain standards and quality checks for automated and manual chamber systems instead of defining one or several standard systems provided by commercial manufacturers in order to define minimum requirements for chamber measurements. This manuscript summarizes the main issues presented in the ICOS protocol and instruction documents describing the requirements and recommendations related to chamber measurements.

METHODOLOGY

A) Automated chamber measurements

Measurements methods and instrumentation

In principle, several technical solutions are available to design an automated chamber system for fluxes of CO₂, CH₄ and N₂O between soil/ecosystem and the atmosphere. They are typically classified into open dynamic chamber (steady-state through-flow) and closed dynamic chamber (non-steady-state through-flow) systems. In open dynamic chambers, the sample air is withdrawn from the chamber to a gas analyser and replacement air with known gas concentration is directed to the chamber to maintain pressure equilibrium. During the chamber closure, the chamber headspace reaches steady-state concentration from which the flux can be calculated. The closed dynamic chamber operates in a fully enclosed mode in which the sample air is continuously drawn from the chamber headspace to a gas analyser and returned back to the chamber, and measures the continuous changes in GHG concentration in the chamber headspace over a short time. The flux is calculated from this change using either a linear or non-linear fit model. For detailed description of the chamber types, see Livingston and Hutchinson (1995) and Pumpanen *et al.* (2009).

Since most of the chamber systems (commercial as well as home-made) used for GHG flux measurements are based on the closed dynamic approach, the recommended standard method for ICOS is a closed dynamic chamber system. Two different ways to design air sampling in closed systems are: (1) the system integrates all required gas analysers in the field, (2) automatic in-situ collection of air samples which are afterwards analysed in the laboratory. Given the fact that this protocol aims to suggest the optimum infrastructure for a period of at least 20 years, we recommend an automated chamber system comprising GHG analysers that can be setup in the field to avoid labour-intensive analyses

in the laboratory and to minimize the running cost. On the other hand, manual measurements are still encouraged to estimate the spatial heterogeneity.

Each measurement technique, design and setup reveals various advantages and disadvantages in comparison to other approaches. The method has construction issues that have to be taken into account regarding the ecosystem to be monitored. The aim of the given specifications is to ensure minimization of potential problems and shortcomings associated with chamber-based flux measurements conducted at ICOS ecosystem stations. A typical chamber system for GHG measurements will consist of the chamber itself, a collar inserted into the ground onto which the chamber is secured, a sampling unit transferring the chamber headspace air sample to a gas analyser, and a controlling unit to operate the chamber system and store the measurement data.

Chamber design

It is almost impossible to define a standard chamber, because different ecosystems require different chamber designs. For example, a small chamber designed for forests with stony soil and small understory vegetation is not suitable for grasslands and croplands with tall plants. Therefore, specific ecosystems require customized solutions.

The chamber design and measurement protocol should aim to minimize the disadvantages of the chamber systems, *e.g.*, changes of the microclimate inside the chamber, such as radiation, precipitation, temperature, wind speed, and litter input. Special attention must be paid to pressure equilibrium between the chamber headspace and the ambient air, in particular, during the closing of the chamber but also during the entire measurement period when air samples are taken from the chamber headspace to avoid bias on chamber air concentration developments over time.

Chamber design requirements and recommendations

The chamber design depends on the purpose of the measurements. The design has to fulfil the following requirements and recommendations:

- 1) Opaque chambers have the advantage that during the short closure period of < 5 min the headspace air temperature does not increase as much as in a transparent chamber, and thereby minimises unintended warming effects on soil components/plants. If transparent chambers are used, the whole chamber (wall and lid) should be painted or covered with tin foil in order to block out sunlight. We recommend to paint it with a white matt colour to avoid possible direct reflection of the sun on nearby radiation sensors. Apart from opaque chambers, measurements with transparent chambers are recommended (but not obligatory) to facilitate the quantification of the contribution of ground vegetation to the net ecosystem exchange (NEE) at sites where the contribution of ground vegetation is relevant (contribution of ground vegetation to NEE >10%).

2) Chamber shapes are commonly cylindrical or rectangular in cross-section, although any chamber shape is acceptable. A cylindrical shape allows better mixing of the enclosed air, while a rectangular shape generates dead space in the top corners of the chamber where enclosed air may not be mixed properly (Livingston and Hutchinson, 1995).

3) The chambers should be fabricated of non-permeable and inert materials, *i.e.* Polyvinylchloride (PVC), Polypropylene (PP), Polyethylene (PE), Acrylonitrile-Butadiene-Styrene (ABS), Polytetrafluoroethylene (PTFE-Teflon), Polymethyl Methacrylate (PMMA), stainless steel or aluminium. The outer colour of chambers should be white.

4) Chambers must be fitted with a vent in order to avoid pressure changes when closing and opening the chambers (Christiansen *et al.*, 2011), but also during the measurements period. The inner diameter of the vent is a function of chamber volume (Hutchinson and Mosier, 1981). Another possible solution is a vent-tube (Xu *et al.*, 2006) in order to achieve the chamber pressure equilibrium, mainly at windy sites.

5) Adequate air mixing must be assured inside the chamber headspace. This can be achieved by the airflow between the chamber and the GHG analyser (the majority of commercial systems) or by installing fan/fans inside of the chamber to achieve air movement similar to the outside averaged wind speed close to ground surface. The optimum seems to be a system where chamber ventilation follows the average wind speed a few minutes before starting the measurements. In case of constant fan speed the ventilation should be gentle and not too strong, an excessive air movement inside the chamber is thought to disrupt the high laminar boundary layer above the soil (Le Dantec *et al.*, 1999; Koskinen *et al.*, 2014). The average speed of air movement inside the chamber should be less than 0.5 m s^{-1} ; measured at four points across the chamber and at half the height of the chamber. The main airstream should not be directed towards the soil to prevent unwanted suppression of gas diffusion from the soil into the chamber atmosphere, or to avoid flushing of soil air to the headspace. Visualization of the movement of the air inside of the chamber can be done using a small source of smoke (*e.g.* cigarette).

Another possibility is to control the fan speed following outside wind conditions using a sensitive ultrasonic anemometer installed close to the ground to have similar conditions inside and outside the chamber. In this case, fan speed should not be changed during one measurement of one chamber – an average speed calculated from previous about 2 min wind speed is recommended.

6) The Venturi effect is the reduction in fluid pressure that results when a fluid flows through a constricted section of a pipe (Bahn *et al.*, 2009; Bain *et al.*, 2005; Davidson *et al.*, 2002; Kutsch *et al.*, 2009). It should be investigated

for each chamber design following the protocol of Bain *et al.* (2005), when the chamber ventilation is switched on. Interactions between the Venturi effects and internal ventilation are complex and not fully clarified. Since turbulence can cause pressure fluctuations over bare soil (without any chamber deployed), which can enhance gas transport, the chamber design can modify these fluctuations in both directions. The optimum seems to be a system where chamber ventilation follows the average wind speed a few minutes before starting the measurements.

7) Collar insertion should assure a good chamber-to-soil seal, however, at the same time it is necessary to minimize the cut of the surface rooting zone in order to avoid trenching effect (see section soil collars).

8) Effects of chamber design on rain and fertilizer addition/spreading inside the measured area have to be minimized as much as possible using proper design and measurement time schedule (see Chamber and system design testing).

9) To prevent damage or cutting of vegetation inside the collar during the closing of the chamber (*e.g.* grasslands and croplands), a thin metal wire mesh disposed along the inner circumference of the collar is recommended.

10) If it is planned to close the chambers for long time ($> 30 \text{ min}$) due to $\text{N}_2\text{O}/\text{CH}_4$ measurement, it is recommended to take into account that the insertion collar depth is generally a function of closure time (De Klein and Harvey, 2012). Therefore, it is necessary to increase the collar insertion depth during its installation.

11) Inlet tubes (pipes) should not be located less than $\frac{1}{2}$ of the chamber height and should be fitted with a net or filter to avoid insects incoming to the measurement system. If tubing is longer than approx. 10 m, its permeability to measured gases must be tested again. To avoid damage, the chamber system should be in a fenced area in areas frequented by large animals (cattle, sheep, wild boar, deer, bear *etc.*).

Auxiliary measurements

Each chamber should be instrumented with sensors for measuring the following variables, whose logging interval should be coordinated with the sampling of the analysers between 0.1 and 1 Hz:

- Air temperature: The position of air temperature sensor should not be too close to the wall or lid to prevent biased values due to surface heating of chamber material. Its main purpose is the measurement of temperature fluctuations during closure time. The sensor should be protected from direct sun light. These data are necessary in the process of flux calculations.

- Soil temperature: Soil temperature should be measured inside each collar; the depth of these measurements depends on the type of ecosystem and soil. For CO_2 we recommend estimating the proper depth in order to synchronize daily courses of soil temperature and soil CO_2

efflux (Graf *et al.*, 2008; Pavelka *et al.*, 2007; Subke and Bahn, 2010). However, following the compulsory measurement depths of soil temperature in the upper soil layer, one measurement at 5 cm is mandatory and one measurement as close to the soil surface as possible is optional.

- **Soil moisture:** A soil water content sensor should be installed close to each collar when a small chamber is used or inside of big chambers. The measurement depth should be close to the soil surface (5 cm) for CO₂ and following the sensor manufacturer recommendations. In special cases, *e.g.* water saturated soils.

If transparent chamber measurements are used it is recommended to measure photosynthetically active radiation (PAR) and relative humidity inside each chamber. We also recommend monitoring the transparency of the chamber and temperature increase during these measurements.

Soil collars

Collars are required to provide an airtight seal between the chamber and the soil surface, and to ensure sufficient stability to the chamber. Soil collars or frames for automated chamber measurements should consist of inert, non-permeable and non-reactive materials *i.e.* PVC, PP, PE, ABS, PTFE-Teflon, PMMA, or stainless steel. Design and size of the collars should minimize disturbances to the root system and shelter effects for rainfall, litter fall or fertilization. Since the optimal collar design depends on the ecosystem type, more specifications are given in the respective sections (Specifications for ecosystem types). To minimize disturbances of the soil and the roots it is pivotal to insert collars as shallow as possible into the soil. The depth of insertion should account for the porosity of the topsoil, as higher porosity requires deeper insertion. In ecosystems with no permanent rooting of plants (*e.g.* agriculture, grasslands), the minimum insertion depth should be 0.03 m and the maximum should be 0.15 m depending on ecosystem type and rooting depth to minimize root disturbance or cutting. In ecosystems with permanent rooting of plants (*e.g.* forest ecosystems), the collars should be placed on top of the humus layer and only pressed firm but gently into the humus to avoid cutting the roots. Then the collars should be anchored steadily into the mineral soil using special anchoring screws that can be adjusted depending on the root development. After the installation of the soil collars measurements of GHG can be started. Acquired data has to be analysed for effects of collar insertion (disturbance) in measured fluxes on the base of principal investigator (PI) experience.

Requirements for GHG analysers

The use of a specific instrument, such as the analyser type or model, is not imposed. However, in order to ensure high quality standard of the chamber measurements, a certain scale of range, precision and accuracy of the instrument will be specified. One of the most important parameters of

the analyser is the short-term stability, which is the drift in baseline concentrations over a timescale of few minutes. The measurement range has to cover all concentrations of monitored GHGs that can appear during the time of measurement. Most of the infrared gas analysers measure also water vapour content. In other words, GHG concentrations in moist air are recorded instead of dry air, due to the absence of an automatic application of the water vapour dilution correction. Brümmer *et al.* (2017) have shown that automated measurements with a high precision quantum cascade absorption laser spectrometer (QCLAS) for N₂O in the field requires only a few minutes of chamber closure, even when fluxes are lower. On the other hand, Korkiakoski *et al.* (2017) demonstrated that very small CH₄ fluxes, varying from uptake to emissions, can be detected with high precision analysers over a short closure time. Therefore, we recommend a minimum closure time of 5 min, to ensure that even very low fluxes can be measured accurately. Using a system that is able to measure the mixing ratios of N₂O, CH₄ and CO₂ in the field should enable continuous measurements for each chamber at least every two hours.

The required parameters for each analyser are:

- Measurement range depends on the time of chamber closure and its volume/surface ratio:
 - CO₂: at least 100 – 2000 ppm
 - CH₄: at least 0 – 10 ppm
 - N₂O: at least 0 – 2 ppm
 - H₂O: at least 0–60 ppt (for water vapour dilution correction);
- Minimal output sampling frequency 0.1 Hz for CO₂
- Minimal output sampling frequency 0.1 Hz for CH₄
- Minimal output sampling frequency 0.1 Hz for N₂O
- Accuracy of the CO₂ analyser should be ≤ 2% of the reading.
- Low root mean square (RMS noise with 1 s signal filtering ≤ 1.5 ppm CO₂, at ambient concentration).
- Accuracy of the CH₄ and N₂O analyser should be minimum 1 ppb in 100 s.
- Another crucial parameter is the stability of the analyser. If any measured gas is injected with constant concentration to the analyser, the output value from the analyser must be stable, changes during 5 min measurements should not be more than 1.5 ppm for CO₂ (Appendix: Fig. 1A), 0.5 ppb for CH₄ and 0.1 ppb for N₂O.

Chamber and system design testing

The following tests should be done for home-made automated chamber systems.

Leakage testing

Each chamber and measurement system must be tested for air-tightness. The testing measurement can be done in the field or in the laboratory conditions provided that concentration of the gas used to test leakages is close to ambient conditions (*ca.* 400 ppm for CO₂). For chamber

air-tightness testing a special frame that is air-tight at the bottom of the chamber (*e.g.* mounted on a metal or plastic sheet from which the chamber was made) has to be constructed. Then the chamber is placed onto the frame in the same way as during field operations. A known CO₂ concentration is injected in the chamber to achieve a concentration similar to that at the end of a field measurement (or higher) (typically the target concentration could be ambient concentration plus approx. 400 ppm, depending on the type of ecosystem). Then the CO₂ concentration inside the chamber is monitored in 10 s intervals for 5 min, which is the standard measurement time (typically from 2 to 5 min, in the case of CO₂ chamber measurement systems; may be more for CH₄ and N₂O measurement systems). The variation caused by possible leakage should be $\leq 3\%$ of the measured flux. This test should be done separately for all the gases measured, CO₂, CH₄ and N₂O.

Impact of pressure changes during chamber closure

Even a small pressure difference between chamber headspace and the atmosphere, as low as 1 Pa, has been shown to cause significant errors to the measured CO₂ efflux (Fang and Moncrieff, 1996; Longdoz *et al.*, 2000; Kutsch *et al.*, 2001). This testing can be realized during the above described leakage testing using the sealed bottom frame. The pressure difference between the chamber headspace and the atmosphere should be monitored continuously during the whole chamber operation, including the closing of the chamber. Overpressure during the closing of the chamber has to be smaller than 10 Pa, and less than 0.1 Pa during the measurement. In the case of overpressure during the chamber closing, an extra pressure equilibrium active vent is recommended in order to prevent pressure alteration dur-

ing chamber closing. Therefore, a hole of about 5 cm in diameter should be made on the top of the chamber. The hole should be closed automatically by a lid few seconds after the chamber closing. The pressure effects caused by chamber closure have to be monitored using a differential pressure transducer during testing phase of the system and documented, and checked in order to facilitate reliable chamber measurements.

Testing of rain intensity altered by the chamber

Effects of the chamber design on rain inside the measured area have to be checked and documented under field condition in an open area, and not underneath a forest canopy, before the installation of the system. A series of rainfall events should be studied by means of at least two simple manual rain samplers of which one will be placed inside the chamber and the other far enough away from the chamber system so they can be considered as independent and not influenced by the chamber (Fig. 1). All samplers will be read out and emptied regularly. The test should be conducted with a minimum of 2 chambers, 3 rainfall events and collecting at least 20 mm cumulative rainfall.

The following measurements have to be conducted:

1. the chambers are permanently open (influence of the rack and the lifted chamber);
2. the chambers will be closed for 3 – 10 min every hour (following typical measurement schedule in the field).

If a deviation from the undisturbed rainfall by more than 20% occurs, the chamber design will not be accepted for long-term measurements within ICOS.

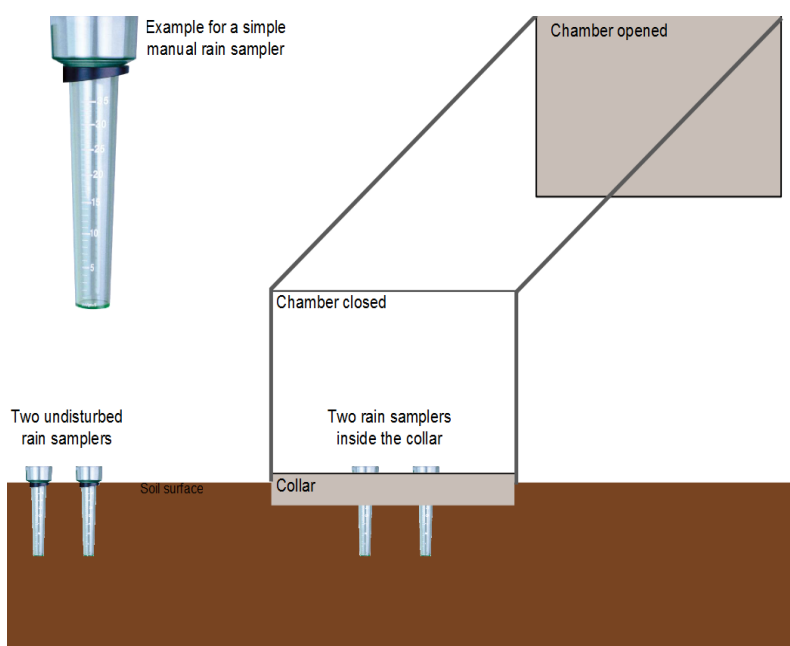


Fig. 1. Scheme for the rainfall.

Testing the shading from solar radiation

The effect of solar radiation shading of an open chamber has to be tested under field conditions in an open area (without canopy). A PAR sensor should be placed in the middle part of the collar, and a second PAR sensor outside of the collar, far enough away from the chamber system that they can be considered as independent and not influenced by the chamber; following the design depicted in Fig. 1 for rain samplers. The measurement should be carried out for a minimum of two full days and include a cloudy day and a sunny day. If the difference in the PAR daily sums between the two sensors is more than 20%, the chamber design will not be accepted for long-term measurements within ICOS.

However, the chamber should be oriented to minimise possible shading of the chamber construction and components to the measured area, when the chamber is opened.

Testing the effect of ventilation on air mixing

The test should be done under field conditions, in the absence of rain and high temperature, avoiding large temperature fluctuation and preferable during overcast periods. The fan should be switched on for at least 24 h in all chambers and then switched off for approximately 24 h in one half of the total number of chambers (three chambers in case that the total number is five chambers). Thereafter, the fan must be switched on again in all chambers and concentration measurements should continue for at least 24 h.

Chamber system calibration and maintenance

The GHG analyser of the chamber system must be calibrated or validated according to the manufacturer recommendations and at least once per year. The chamber system should be controlled regarding chamber operations and quick leakage testing (by breathing to critical parts of the system, sealing of the chamber closing) once per month in order to avoid any malfunction of the system.

Spatial and temporal sampling design

Spatial sampling strategy

Automated chamber system allows studying the dynamics of GHG exchange at a high temporal resolution for extended periods of time but due to a limited number of automatic chambers it is not possible to fully explore the spatial variation at the full EC footprint area. Therefore, five (six in special cases; see Specifications for ecosystem types) sampling points/chambers, depending on type and occurrence of vegetation, were chosen as the required minimum number for the automatic chamber systems. This decision is based on a compromise between economic reasons and scientific points of view. The automatic chambers should be located within the EC footprint area but not in the main wind direction in order to avoid disturbance to the EC measurement. Also, the chambers should cover the main representative parts of the soil surfaces (see Specifications

for ecosystem types) according to the studied ecosystem. In case of no predominant wind direction, it is possible to install the chambers in four different quadrants around the EC tower to cover the EC footprint.

To quantify the spatial heterogeneity of GHG fluxes a survey with manual chamber campaign is recommended (see Specifications for ecosystem types for the manual measurements in specific ecosystems). These sampling points should be located in the EC footprint area.

In order to minimize the chamber disturbances to the soil and to better cover the spatial variability, the automated chamber system must comprise of twice as many collars than chambers so that each chamber is manually moved between at least two collars at least once a year. However, not all collars should be moved at the same time as shown in the following example, where five chambers are moved between ten collars in four steps (Fig. 2). Moving only two or three chambers at one step, guarantees continuous data for the other chambers and the possibility to relate the fluxes from different collars to each other. For “relaxing positions”, set of special short collars should be made in order to minimize influence of physical properties as solar radiation, precipitation and litter fall input. The role of the “relaxing collars” is to keep the original measurement position and minimize soil disturbance (roots cutting) after reinstallation of the measuring collar to the original position. The height of the relaxing collar should be equal to the insertion of the measuring collar. It means the upper edge of the relaxing collar should be at the same level as soil surface. In order to facilitate visibility of the relaxing position it is recommended to mark each position with a small flag with north direction about 20 cm from the collar. Collar

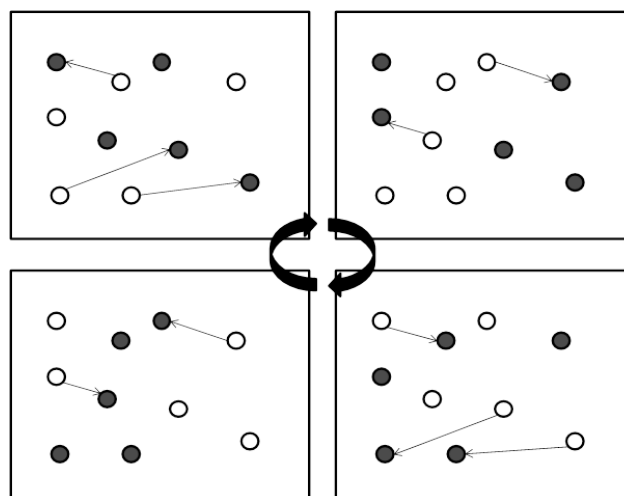


Fig. 2. Example for rotation of 5 permanent chambers on 10 collars. Collars without chamber are in white circle and collars with chamber are black circle. The collars without chamber (relaxing collar) should be measured regularly in campaigns. The narrow arrows indicate the change of relaxing collar position while the wide arrows the rotation change during a year.

positions for automated measurements should be changed preferably during reinstallation of the system after winter period, in accordance of measurement and relaxing collars scheme description (see spatial sampling strategy).

Special attention should be paid to the installation of tall chambers designed for measurements in ecosystems with tall plants (*e.g.* grassland, wetland or cropland). Tall chambers that are lifted upwards can disturb the turbulence structure inside the footprint. Notwithstanding, the best arrangement covers those sub-habitat components that have the highest representativeness and are expected to contribute to the bulk of the exchange. The number of used chambers in different habitats should respect the ratio of the habitats area in the footprint (Merbold *et al.*, 2011).

Concerning chamber GHG measurements in winter, measurements should be continued during winter if possible. There exist chamber designs specifically constructed to tackle most of the challenges related to wintertime (Koskinen *et al.*, 2014; Korkiakoski *et al.*, 2017). For example, supporting the collar by separate legs, which allows the vertical lifting of the whole chamber and installing extension, collars between the frame and bottom collar prior to snowfall significantly lessen the disturbance to the snowpack. Relevant CH₄ and N₂O fluxes may occur in winter, particularly in peatlands (Korkiakoski *et al.*, 2017), but also in other ecosystems with increased mineralization of soil organic matter during the freezing and thawing of soil. If chamber measurements prove to be too challenging, we recommend using other techniques to reasonably identify the spatial and temporal heterogeneity of GHG fluxes during winter. These include a gradient method within the snow pack (Merbold *et al.*, 2013; Suzuki *et al.*, 2006; Mariko *et al.*, 2000) or the soil (Pumpanen *et al.*, 2008; Pihlatie *et al.*, 2007). Therefore, if it is not possible to continue chamber measurements through the whole winter, we recommend performing chamber measurements as long as the environmental conditions (absence of snow or flooding, particularly) allow to do so. Particularly we encourage researchers to cover the transition periods between the seasons, *e.g.* fall to winter including the first snow cover and also potential freeze-thaw events in early winter and spring. This is to account for potential GHG pulses, which may be caused by increased mineralization and/or increase or reduction in water content in the soil.

Temporal sampling strategy

Automated chamber systems allow studying dynamics of GHG fluxes in high resolution for extended periods of time. Therefore, it is expected that the whole vegetation season will be monitored. The minimum time resolution for individual GHG flux measurements should be one measurement per hour/per gas per each chamber. Using a system that is able to measure the mixing ratios of N₂O, CH₄ and CO₂ in the field should enable hourly measurements of

each chamber per day. In case of higher number of chambers (more than five) the minimum time resolution for all measured GHG can be prolonged up to 2 h per each chamber. As stated in the previous section, in regions where the winter period (*e.g.* Nordic countries, mountain areas) has extreme environmental conditions (low temperatures, high snow cover, *etc.*) automated measurements of GHG fluxes are not expected but encouraged during winter months.

Companion variables

Beside soil-meteorological variables such as soil temperature and moisture, vegetation characteristics inside the collars (including relaxing collars) should be monitored (species identification, cover fraction, LAI, vegetation height, digital photos) twice a year (at the beginning of the growing season and at the maximum of understory vegetation) in order to document the possible long-term impact by the chambers. Moreover, five-control plots, apart from the relaxing ones, should also be monitored. They should be located in representative positions up to five metres from the measuring/relaxing collars.

B) Manual chamber measurements

Although being labour-intensive, manual chamber measurements are simple, low cost and therefore conducted by a multitude of researchers worldwide (Appendix: Table A2). Even though regular manual chamber measurements are not mandatory within ICOS they can add valuable information and data on soil GHG exchange:

- in case of limited numbers of automatic chambers (a minimum of 5 chambers was defined) additional manual chamber measurements are recommended to characterize spatial variability of soil GHG exchange in the EC footprint area;
- manual chamber measurements can complement automatic measurements at times when automatic chamber systems cannot be operated (*e.g.* wintertime, intensive field preparation);
- for all sites without automatic measuring systems regular manual chamber measurements are recommended for estimating annual sink and/or source strengths of soil GHG exchange.

Therefore, here we aim on reflecting main issues of sampling design, measuring procedure and GHG concentration analysis, in order to harmonize manual chamber measurements of soil GHG exchange across ICOS sites.

Measurement methods and instrumentation

Chamber design

A standard manual chamber is almost impossible to be defined, because different ecosystems require different chamber designs and different research groups already use different kinds of chambers (Appendix: Table A2).

If applied in combination with an automatic measuring system, manual chambers and collars ideally should have the same dimension and should be constructed from the same material as automatic chambers. If this is not feasible, manual chamber and collar designs should follow the technical requirements given for automatic chamber systems; most importantly taking into account, the minimum chamber size of 0.2 x 0.2 m or an equivalent covered ground area. As outlined for automatic chamber measuring systems chamber/collar systems should be tested against leakages and pressure changes during sampling. In case of manual survey using gas chromatography, the pressure change issue can be easily minimized by a relatively high chamber headspace volume compared to total volume of sample air taken for GHG concentration analysis (factor of at least 25).

In case those manual chamber measurements are conducted to complement automatic chamber measurements in wintertime, note that snowy conditions require a different measuring setup. The most commonly used method is a snowpack concentration gradient method where the flux is calculated from gas concentration gradients and snow density. Chamber methods have been applied by inserting the chamber on top of the snow or by directly inserting the chamber into the snow (with or without an extension). The snowpack concentration gradient method involves uncertainties in gas diffusion and snow density measurements, while the chamber method may give a biased estimate of the flux due to undefined source area in the snow beneath the chamber. Selection of the most suitable method, as well as the reasonable frequency of winter measurements in snowy conditions are site specific and need to be judged by the site PI. We anticipate future research targeting improvements in snow flux measurements but currently suggest the snow gas concentration gradient method to be preferable used at significant heights of snowpack.

Auxiliary measurements

For calculation of molar volume (term of the flux calculation routine) measurements of temperature inside the closed chamber and air pressure at the measurements site are mandatory. Most suitable are mobile temperature sensors with internal loggers which can be placed inside any chamber or at least in a subset of three chambers.

Measurements such as soil moisture and soil temperature are recommended to be taken with portable probes at any chamber position before sampling in order to allow correlation of soil GHG fluxes with environmental parameters. Further measurements such as vegetation dynamics/ characteristics (plant composition, height *etc.*) should be taken regularly and should also be documented by photographs.

Spatial and temporal sampling design

Characterization of soil GHG exchange in the footprint area

Characterization of soil GHG fluxes in the footprint area should be based on a number of at least 25 positions. If root disturbance is an issue, all collars should be permanently installed according to the recommendations given in the specifications for ecosystem types in the automatic chamber section. Collar placement should representatively cover any heterogeneity (soil, vegetation, topography *etc.*) in the EC footprint area. Manual chamber measurements should, wherever applicable, cover seasonal changes (winter, spring, summer and autumn) and ecosystem specific events such as re-wetting, freeze-thaw cycles and fertilization/harvest events. Due to potential diurnal patterns of soil GHG emissions, it is recommended to do measurements every 4 h (*e.g.* 06:00, 10:00, 14:00, 18:00; 22:00; 02:00) and a minimum of 4 measurements during the day (*e.g.* 6:00, 10:00; 14:00; 18:00), for more details concerning chamber measurements time schedule see Darenova *et al.*, 2014. Particularly, night-time measurements are very valuable since a lot of night-time EC data is rejected due to low turbulence.

Note that if an infrared gas analyser is available for automatic chamber measurements, the same sensor can be connected to a single chamber with sufficiently long sampling tubing (approx. 10 m), which can be subsequently placed at all collars in the footprint area ("fast box" approach: Hensen *et al.*, 2006).

Estimation of sink and/or source strengths of soil GHG exchange

At sites without automatic measuring systems, regular manual chamber measurements are recommended for estimating the annual sink and/ or source strengths of soil GHG exchange. Following the minimum requirements of the automatic chamber measurements at least 5 collars should be representatively placed in the footprint area. Measurements should be conducted at least weekly, but more often (daily – every other day) during times of expected elevated fluxes. There is evidence from several studies that the most suitable sampling time for GHG emissions is 09:00 – 10:00 h when fluxes best represent the daily mean (Darenova *et al.*, 2014). However, since this can vary across ecosystems and seasons, it is recommended to seasonally (winter, spring, summer, autumn, including ecosystem specific events) characterize possible diurnal flux patterns by sub-daily measurements in 4-h time intervals (*e.g.* 06:00, 10:00, 14:00, 18:00; 22:00; 02:00) but at least 4 measurements during the day (*e.g.* 6:00, 10:00; 14:00; 18:00). This characterization can further guide definition of flexible sampling times best representing mean daily emissions, to avoid biased estimation of annual GHG exchange budgets. Generally, the relevancy and frequency of these

measurements is ecosystem and management specific and therefore best to be decided by the site PI. Note that diurnal patterns can be insignificant *e.g.* in cold (except freeze-thaw) and dry periods.

Sampling procedure

For soil respiration the use of an infrared gas analyser (IRGA) with circulating chamber air *via* outlet and inlet tubing is recommended. For N₂O and CH₄ exchange the chamber air can be sampled with syringes at minimum 4 times over the chamber closure period. In general, chamber closure time should be kept as short as possible and should not exceed 45 min. Ideally, measurement of soil CO₂ and N₂O/CH₄ fluxes can be combined, *i.e.* short-term IRGA measurements terminated at CO₂ increase of 20–100 ppm followed by syringe sampling ($t_0 = 2\text{--}5$ min, $t_1 = 15$ min, $t_2 = 30$ min, $t_3 = 45$ min). This would require sequentially closing of manual chambers. IRGA inlets and outlets should be easy and quick to connect. The chambers' sample air outlet should be equipped with stopcocks so that the sampling line can be closed after termination of IRGA measurements and the inlet can be further used for the syringe sampling. Number of chambers to be sampled at the same time (*e.g.* sets of 5) mainly depends of man power and distance between the chambers. In case of any constraints with the above sampling procedure, separate sampling of CO₂ and N₂O/CH₄ emissions is recommended.

If analytical capacities are an issue (*e.g.* in case of investigating spatial variability of soil GHG fluxes in the footprint area), the gas sample pooling technique may be helpful. It proposes to collect composite gas samples from several chambers instead of the conventional practice of analysing samples from chambers individually (Arias-Navarro *et al.*, 2013).

To minimize septum penetration, use of stopcocks (also for syringe sampling) is highly recommended. Syringe samples need to be transferred into gas sample containers (vials) for further analysis by gas chromatography or laser spectroscopy. Vials are recommended to be evacuated (< 100 Pa) and additionally flushed with sampling air at least once the vial's volume. To avoid dilution with ambient air vials should be over pressurized by at least the sample volume used for gas chromatographic (GC) analysis.

Quality control for GHG concentration analysis with gas chromatography

In general, gas chromatographs are equipped with an Flame Ionization Detector (FID) for CH₄ and an Electron Capture Detector (ECD) for N₂O concentration analyses. In addition, CO₂ concentrations can be detected either by use of a methanizer and FID or by a Thermal Conductivity Detector (TCD). An important issue to be considered in terms of quality control is adequate separation of N₂O and CO₂ since they can have similar retention times when using *e.g.* porous polymer columns (HayeSep) before the ECD.

Because of non-linearity of ECDs at high N₂O concentrations (>1000 ppb, ECD dependent, should be checked by the user), a thorough multipoint calibration is recommended. In normal operation an adequate (about 20% of analysed samples) number of standards for calibrating the GC system is required *e.g.* to cope with temporal drifts.

Air sample containers with caps need to be leak-proof, clean and made of material(s) which do not react with N₂O and CH₄ (CO₂) *e.g.* glass vials (Exetainer®, Labco Limited, High Wycombe, UK). The container should remain gas-tight after sample transfer to prevent sample dilution during storage until analysis. Such glass vials have screw-on plastic caps with rubber septa. Experience shows that gas tightness is achieved when the cap is screwed on 'finger tight', followed by another quarter-turn. Under pressure in evacuated vials allows quality check of vial tightness while the sample is transferred from the syringe and remaining overpressure allows a potential quality check during storage. Rochette and Bertrand (2003) report and discuss results of a comparison of polypropylene syringes and glass vials.

For initial quality check of air sample containers and GC performance it is suggested to perform the following test:

Fill 40 air sample containers with calibration standard (*e.g.* CO₂, N₂O, CH₄, synthetic air mixture), if possible 20 each in two different concentrations (*i.e.* ambient and higher/ lower than ambient). Analyse 5 ambient and 5 different from ambient after 1, 2, 3 and 4 weeks of storage. Evaluate results of these samples with analyses of 10 additional vials (with same standards) which are filled directly before being sampled by the gas chromatograph system. The test reveals if there are problems of sample dilution during storage and characterization of temporal stability of the gas chromatograph system.

After manual chamber measurements are conducted, an additional test with standard gas provided in unknown concentrations by a central lab is suggested for further quality control of the individual partner sampling procedures.

C) Specifications for ecosystem types

Croplands

Measurements of CO₂ effluxes are very useful for all croplands, while measurements of N₂O and CH₄ are restricted to sites where fluxes of these gases are relevant. This should be verified with a measurement campaign during a period when the fluxes are expected to be high. Chamber design should follow the general requirements mentioned above. CO₂ should be measured automatically within the same system as N₂O. Crops should be included for the purpose of direct measurements of ecosystem CO₂ efflux. In case it is not possible to measure with vegetation

due to technical reason, CO₂ should be measured automatically on bare soil with no plants inside the chamber to get the soil component of CO₂ efflux. This can be done in a parallel approach with a system of small chambers. Due to the commonly observed low proportion of CH₄ on the total GHG budget of agricultural sites, automated measurements of CH₄ are not mandatory. To identify a site's general exchange characteristics and levels, CH₄ measurements should be conducted as a part of the manual chamber campaigns (see below). If automated measurements of any GHG will be carried out with plants and on bare soil, the number of chambers should be at least three per variant (three chambers with plants and three chambers on bare soil). In the case of only one variant at least five chambers must be used.

Automated measurements of CO₂ and N₂O (plants included in chamber)

- Automated chambers for the measurement of CO₂ and N₂O should cover area from 0.03 to 1 m². If square shaped chambers are used the minimum size of covered ground area should be 0.2 x 0.2 m.

- The chamber height should be at least be 0.3 m, but should in any case accommodate crop height. Extensions can be attached to the regular chamber during the growing season, but should only be used if necessary to keep chamber dimensions as feasible as possible and to prevent insufficient air mixing inside the chamber.

- Soil collars should be inserted at least 0.09 m into the ground and extend no more than 0.05 m above the surface. Nevertheless, collar insertion should be minimized in order to avoid root disturbance. Ideally, collars will be inserted immediately after sowing of the crop to allow roots to grow without later disturbance.

- A minimum standard of three opaque chambers is required for the combined CO₂ and N₂O measurements where plants are included.

- Measurements of investigated GHG and data collection should be started immediately after collar installation.

Automated measurements of CO₂ (plants not included in chamber)

- Automated measurements of soil CO₂ efflux should be conducted with chambers covering a ground area between 0.03 and 1 m².

- Heterogeneity of root density should be considered by putting chambers in different distances from plant rows (from a few centimetres from the nearest plant to middle part of space between the rows).

- As a minimum standard three opaque chambers are required for soil CO₂ efflux measurements on bare soil.

- Measurements of investigated GHG and data collection should be started immediately after collar installation.

Manual measurements of CO₂, N₂O and CH₄

- Chambers for manual CO₂, N₂O and CH₄ measurements should have the same dimensions as chambers for the automated measurements that include plants if possible.

- Soil collars should be installed at least 24 h before the first measurements (Bahn *et al.* 2009).

- Manual chamber measurements should be made every 2-3 years on at least 25 different positions and this at least two times a day when maximum and minimum CO₂ fluxes can be expected within the EC footprint.

- It is recommended to undertake these campaigns when significant GHG fluxes are expected and during appropriate conditions for the EC measurements.

General operating instructions for chamber deployment

- In case no big chamber system, which covers taller plants, is available, smaller chambers may be used and placed between the rows of plants is possible (*e.g.*, maize, sunflower, *etc.*). If there is not enough space for a proper installation (*e.g.*, between rape seed plants, wheat, barley, *etc.*), single plants should be removed directly after germination to assure measurements under conditions that are as natural as possible. Disturbance of plots should be minimized.

- Site operators should ensure a so-called 'conditional random distribution' of chambers. This means that knowledge about site characteristics, particularly soil properties, is required to cover the heterogeneity within a field. For example, if some parts of the land area are dominated by clay soil, others by silt and/or sand, the total number of available chambers should be evenly distributed to the respective soil type class (*e.g.*, 2 to the sand, 2 to the silt, and 1 to the clay-dominated section of the field if 5 chambers are available) and randomly distributed within each class.

- Collar positions for automated measurements should be changed once a year, preferably after soil preparation.

- The following information is required:

- Date and time of collar installation.
- Date and time of measurement start.
- Date of fertilizer application plus fertilizer type and quantity.
- Numbering of collars and chambers. As all sampling positions change once a year, all measurement spots, *i.e.* collars, should be numbered consecutively to ensure a specific ID for each location. Chambers, however, should have their own fixed ID. The location of the collars (GPS coordinates or position relative to the EC tower) should be documented.
- Documentation of snow accumulation, ice, and other disturbances inside or outside the chamber as well as any information or estimates of chamber volume modification due to plants, snow, *etc.*

- Chambers may be left on the field during fertilizer application if the farmer is able to drive around the measurement plots with his fertilizer apparatus without causing any significant disturbance. In case it is not possible, an equivalent amount of fertilizer has to be applied manually inside and directly next to each chamber. In case any practical reasons (*e.g.*, guy wires, *etc.*) prevent farmers from fertilizer application, chambers and soil frames should be removed prior to field operation and repositioned as soon as possible thereafter.

- Chambers and soil frames should in any case be removed under management activities like ploughing or grubbing.

- If the field site is known for the occurrence of mice or similar animals (*e.g.* frogs, insects), the site operator/PI should (1) try to avoid the entering into the chambers by setting up a fence or traps, (2) displace or eliminate the animals, or (3) move the chamber.

Forests

Chamber measurements have been intensively used in forest ecosystems for estimation of soil surface CO₂ efflux for the last decades, while not long ago they started to be applied for N₂O and CH₄ flux measurements in this ecosystem type. Chamber measurements of soil CO₂ effluxes are compulsory for all forest sites. CH₄ and N₂O exchange is generally low in forests on mineral soils but can be substantial in forest on organic soils. Therefore, due to this high variability it is recommended to measure fluxes of all three GHGs (CO₂, N₂O and CH₄) with an automated chamber system in relevant ecosystems, such as floodplain forest, forested peatland, *etc.* Chamber design should follow the general requirements as mentioned above. However, chamber size may vary depending on understory vegetation of the studied forest. The CO₂ flux in forest should be measured automatically on soil in order to obtain the soil CO₂ efflux. If automated measurements are carried out with and without understory vegetation, the number of chambers should be at least three per variant (three chambers with plants and three chambers without plants). In case of only one variant, the minimum number of chambers is five.

Automated measurements of CO₂, N₂O and CH₄ (understory vegetation included in chamber)

- Automated chambers for the measurement of CO₂, N₂O and CH₄ should cover area from 0.03 to 1 m². If square shaped chambers are used the minimum size of covered ground area should be 0.2 x 0.2 m.

- The chamber height should be at least 0.1 m, but should in any case accommodate the understory vegetation height.

- Measured plots should be representative for the EC footprint area.

- Soil collars should be inserted at least 0.03 m into the ground (measured from the top of the humus layer, if applicable) in accordance to porosity of topsoil (higher

porosity, deeper collar insertion) and extend no more than 0.2 m above the surface. Height of above ground part of the collars should be chosen with regard to the height of litter layer during litter fall period. Nevertheless, collar insertion should be minimized in order to avoid root disturbance or cutting.

- Heterogeneity of root density should be considered by putting chambers in different distance from trees.

- In case of combination of automated chamber system for measurements of two or more GHGs, a minimum standard of five chambers is required where plants are included.

- Measurements of investigated GHG and data collection should be started immediately after collar installation.

Automated measurements of CO₂ (without understory vegetation in chamber)

- Automated measurements of soil CO₂ efflux should be conducted with chambers covering a ground area between 0.03 and 1 m².

- Heterogeneity of root density should be considered by putting chambers in different distance from trees.

- As minimum standard of three opaque chambers are required for soil CO₂ efflux measurements on soil without understory vegetation.

- Measurements of investigated GHG and data collection should be started immediately after collar installation.

Manual measurements of CO₂

- The campaigns should be made every 2-3 years on at least 25 different positions and at least two times a day when maximum and minimum CO₂ fluxes can be expected within the footprint of the EC tower.

- Chambers for manual CO₂ flux measurements should have the same dimensions as chambers for the automated measurements that include plants or should be designed to allow measurements including vegetation, if applicable.

- The collars should be placed in a transect with regular distances between adjacent points. The transect should be located within the EC footprint and follow the fall line direction if the footprint covers sloping terrain. If the footprint consists of heterogeneous patches, chamber locations should cover all different patches.

- Soil collars should be installed at least 24 h before the start of the measurements (Bahn *et al.* 2009).

- It is recommended to undertake these campaigns when significant CO₂ fluxes are expected and during appropriate conditions for the EC measurements.

General operating instructions for chamber deployment

- Site operators should ensure a so-called 'conditional random distribution' of chambers. This means that knowledge about site characteristics, particularly soil properties, is required to cover the soil heterogeneity of a forest. Collar positions for automated measurements should be changed periodically according to the instructions in the experimental design chapter.

- The following set of information is required:
 - Date of collar installation.
 - Date of measurement start.
 - Any management carried out in the forest site should be documented, such as partial harvest, clearing, fertilization *etc.*
 - Numbering of collars and chambers: As all sampling positions change, all measurement plots, *i.e.* collars, should be given a unique ID. Chambers, however, should have their own fixed ID. The location of the collars (GPS coordinates or position relative to the EC tower) should be documented.
 - Documentation of snow or ice accumulation, or other disturbances inside or outside the chamber, as well as information of chamber volume modification due to understory vegetation, snow, *etc.*
- If the forest site is known for the occurrence of ants and/or mice (including similar animals, *e.g.* frogs, insects), the site operator/PI should (1) try to avoid the entering into the chambers by setting up a fence or traps, (2) displace or eliminate the animals or (3) move the chamber.

Peatlands and wetlands

Peatlands are here defined as any histosol in which the surface is dominated by a continuous but biological cover. Here, managed peatlands such as forested or agricultural ones are excluded, and belong to either the forest or the cropland/grassland category. Opaque chamber measurements provide temperature response data, which helps in parameterizing functions that are capable of modelling total ecosystem respiration. This is particularly important in northern latitude ecosystems with very short duration of dark night conditions during summer. Relevant CH₄ fluxes in peatlands might occur when water tables are high. Boardwalks/paths are necessary to avoid disturbance and losses of gases from the peat or soil. Five chambers must be used for automated GHG measurements in peatland or wetland.

Automated measurements of CO₂, N₂O and CH₄ (plants included in chamber)

- Automated chambers for the measurement of CO₂, N₂O and CH₄ should cover area from 0.03 to 1 m². If square shaped chambers are used the minimum size of covered ground area should be 0.2 x 0.2 m.
- The chamber height should be at least 0.1 m, but should in any case accommodate the vegetation height. Extensions can be attached to the regular chamber during the growing season, but should be used only if necessary to keep chamber dimensions as feasible as possible and to prevent insufficient air mixing inside the chamber.
- Soil collars should reach at least 0.09 m into the ground and extend no more than 0.30 m above the soil surface. The collar depth must be great enough to prevent

leakage of gases, but should avoid cutting the roots as much as possible. The ratio of the above ground height and diameter should be equal or smaller than 0.5.

- A minimum standard of three opaque chambers is required for the combined CO₂, CH₄ and N₂O measurements in plots with plants included.
- Opaque chambers are obligatory, transparent chambers can be used if measurements of net ecosystem exchange are intended.
- Measurements of investigated GHG and data collection should be started immediately after collar installation.

Automated measurements of CO₂ (plants not included)

- Automated measurements of soil CO₂ efflux should be conducted with chambers covering a ground area between 0.03 and 1 m².
- As minimum standard of three opaque chambers are required for CO₂ soil efflux measurements on peatland/wetland.
- Measurements of investigated GHG and data collection should be started immediately after collar installation.

Manual measurements of CO₂, N₂O and CH₄

- Chambers for manual CO₂, N₂O and CH₄ flux measurements should have the same dimensions as chambers for the automated measurements that include plants or should be designed to allow measurements including vegetation, if applicable.
- Soil collars should be installed at least 24 h before the first measurements (Bahn *et al.*, 2009).
- Manual chamber measurements should be made every 2-3 years on at least 25 different positions and at least two times a day when maximum and minimum CO₂ fluxes can be expected within the footprint of the EC tower.
- The collars should be placed in a transect with regular distances between adjacent points. The transect should be located within the EC footprint and follow the fall line direction if the footprint covers sloping terrain. If the footprint consists of heterogeneous patches, the transect should cover all different patches. In case of vulnerable vegetation exists the transect can follow a utility boardwalk.
- It is recommended to undertake these campaigns when GHG fluxes are expected and during appropriate conditions for the EC measurements.

General operating instructions for chamber deployment

- In case no big chamber system, which covers taller plants, is available, smaller chambers may be used and placed between the tussocks of plants if possible (*e.g.* *Carex sp.*). If there is not enough space for a proper installation, single plants should be removed to assure measurements under conditions that are as natural as possible. Disturbance of plots should be minimized.

- Site operators should ensure a so-called ‘conditional random distribution’ of chambers of automated system. This means that knowledge about site characteristics, particularly soil properties, is required to cover the heterogeneity of a field. For example, if some parts of the land have lower altitude and therefore water table depth is shallower, others have deeper water table, the total number of available chambers should be evenly distributed to the respective soil type class (*e.g.*, 2 to the wetter, 2 to the drier, and 1 to the transition section of the field if 5 chambers are available) and randomly distributed within each class.

- Collar positions for automated measurements should be changed once a year, preferably after winter period.

- We recommend that the access paths to the automated chambers should be prepared with boardwalks in order to minimize the disturbance around the chambers.

- The following set of information is required:

- Date of collar installation.
- Date of measurement start.
- Numbering of collars and chambers. As all sampling positions change once a year, all measurement spots, *i.e.* collars, should be numbered consecutively to ensure a specific ID for each location. Chambers, however, should have their own static ID. The location of the collars (GPS coordinates or position relative to the EC tower) should be documented.
- Documentation of snow accumulation, ice, and other disturbances inside or outside the chamber as well as any information or estimates of chamber volume modification due to plants, snow, *etc.*
- If the field site is known for the occurrence of mice or similar animals, the site operator/PI should (1) try to avoid the entering into the chambers by setting up a fence or traps, (2) displace or eliminate the animals, or (3) move the chamber.

Grasslands

Grasslands are one of the dominant land use types in Europe. Most grasslands in Europe are managed for feeding domestic herbivores, either directly by grazing or through forage production as hay or silage. Grasslands contribute to the biosphere-atmosphere exchange of radioactively active trace gases, with fluxes intimately linked to management practices. Concerning the three GHGs that are exchanged by grasslands, CO₂ is exchanged with the soil and vegetation, N₂O is emitted by soils and livestock grazing on the grassland emits CH₄. If automated measurements are carried out with plants and on bare soil, the number of chambers should be at least three per variant (three chambers with plants and three chambers on bare soil). In case of only one variant, at least five chambers must be used.

Automated measurements of CO₂, N₂O and CH₄ (plants included in chamber)

- Automated chambers for the measurement of CO₂, N₂O and CH₄ should cover area from 0.03 to 1 m². If square shaped chambers are used the minimum size of covered ground area should be 0.2 x 0.2 m.

- The chamber height should be at least 0.1 m, but should in any case accommodate the vegetation height. Extensions can be attached to the regular chamber during the growing season, but should only be used if necessary to keep chamber dimensions as feasible as possible and to prevent insufficient air mixing inside the chamber.

- Soil collars should reach at least 0.05 m into the ground and extend no more than 0.30 m above the surface. The ratio of the above ground height and diameter should be equal or smaller than 0.5. Nevertheless, collar insertion should be minimized in order to avoid root disturbance.

- A minimum standard of three opaque chambers is required for the combined CO₂, CH₄ and N₂O measurements.

- Opaque chambers are obligatory, transparent chambers can be used if measurements of net ecosystem exchange are intended.

- Measurements of investigated GHG and data collection should be started immediately after collar installation.

Automated measurements of CO₂ (plants not included)

- Automated measurements of soil CO₂ efflux should be conducted with chambers covering a ground area between 0.03 and 1 m².

- Measurements position should be located in spots naturally without vegetation (among grass turfs).

- As minimum standard three opaque chambers are required for CO₂ soil efflux measurements on bare soil.

- Measurements of investigated GHG and data collection should be started immediately after collar installation.

Manual measurements of CO₂, N₂O and CH₄

- Chambers for manual CO₂, N₂O and CH₄ measurements should have the same dimensions as chambers for the automated measurements that include plants or should be designed to allow measurements including vegetation, if applicable.

- Soil collars should be installed at least 24 h before start measurements (Bahn *et al.*, 2009).

- Manual chamber measurements should be made every 2–3 years on at least 25 different positions and at least two times a day when maximum and minimum CO₂ fluxes can be expected within the footprint of the EC tower.

- The collars should be placed in a transect with regular distances between adjacent points. The transect should be located within the EC footprint and follow the fall line direction if the footprint covers sloping terrain. If the foot-

print consists of heterogeneous patches, the transect should cover all different patches. In case of vulnerable vegetation exists the transect can follow a utility boardwalk.

- It is recommended to undertake these campaigns when GHG fluxes are expected and during appropriate conditions for the EC measurements.

General operating instructions for chamber deployment

- Site operators should ensure a so-called ‘conditional random distribution’ of chambers automated system. This means that knowledge about site characteristics, particularly soil properties, is required to cover the heterogeneity of a field. For example, if some parts of the land have lower altitude and therefore water table depth is shallower, others have deeper water table, the total number of available chambers should be evenly distributed to the respective soil type class (*e.g.*, 2 to the wetter, 2 to the drier, and 1 to the transition section of the field if 5 chambers are available) and randomly distributed within each class.

- The following set of information is required in addition to the ancillary data submitted anyway (along with the dataset itself):

- Date of collar installation.
- Date of measurement start.
- Numbering of collars and chambers. As all sampling positions change once a year, all measurement spots, *i.e.* collars, should be numbered consecutively to ensure a specific ID for each location. Chambers, however, should have their own static ID. The location of the collars (GPS coordinates or position relative to the EC tower) should be documented.
- Documentation of snow accumulation, ice, and other disturbances inside or outside the chamber as well as any information or estimates of chamber volume modification due to plants, snow, *etc.*

- Chambers may be left on the field during grassland harvesting/mowing period if the farmer is able to drive around the measurement plots with his harvesting machine without causing any significant disturbance. In case it is not possible, chambers and soil frames should be removed prior to field operation and repositioned as soon as possible.

- If the field site is known for the occurrence of mice or similar animals, the site operator/PI should (1) try to avoid the entering into the chambers by setting up a fence or traps, (2) displace or eliminate the animals, or (3) move the chamber.

D) Final dataset and flux calculation

Long-term research infrastructures have specific requirements for documentation and flux calculation. Since future research might improve methods for flux calculation, or current efforts (Parkin and Venterea, 2010; De Klein and Harvey, 2012) might lead to an international standard, it is crucial that all raw data from all flux measurements are pro-

vided to the central database allowing to recalculate fluxes easily as methods improve or change. Furthermore, it is needed flux calculations to be reproducible and comparable.

Generally, GHG fluxes measured by the chamber method are often represented in different units. Due to standardization, GHG fluxes must be reported in ($\mu\text{mol m}^{-2} \text{s}^{-1}$) for CO_2 and ($\text{nmol m}^{-2} \text{s}^{-1}$) for CH_4 and N_2O . Annual budgets units must be for CO_2 , CH_4 and N_2O in $\text{g CO}_2\text{-C m}^{-2} \text{y}^{-1}$, $\text{g CH}_4\text{-C m}^{-2} \text{y}^{-1}$ and $\text{kg N}_2\text{O-N ha}^{-1} \text{y}^{-1}$, respectively. To calculate the fluxes of any studied GHG it is necessary to know different variables such as concentration of the monitored GHG and auxiliary data (*e.g.* air temperature inside of the chamber, air pressure and volume of the chamber system). Within ICOS flux calculations of the monitored GHG by the chamber method will be done centrally by the Ecosystem Thematic Centre (ETC).

Required raw data for flux calculation

- Flux calculation requires the following raw data:
 - Date and time of measurements with precision in seconds
 - Concentration in ppmv (CO_2) or ppbv (N_2O , CH_4) in dry-air mole fraction, in automated systems measured with a frequency of 0.1 Hz or faster.
 - Air temperature inside the chamber ($^{\circ}\text{C}$).
 - Air pressure (Pa)
 - Water vapour concentration in the analyser cell, if possible
 - Effective system volume (m^3). This is total volume of the chamber:
 - plus air volume of the collar (calculated from height measurements at 9 points of a regular grid, measured at least twice a year and after frames have been moved/installed)
 - plus internal volume of tubing, filters, switching valves analyser and all other parts of measuring line
 - minus volume of equipment installed inside the chamber (can be neglected if estimated to be less than 1% of volume)
 - minus snow volume (snow is considered part of the soil)
 - minus the vegetation volume where relevant.
 - Area covered by the chamber in m^2
 - Additional data that identify the flux measurement:
 - Site ID,
 - Collar ID,
 - Chamber ID,
 - Starting time of flux measurement (YYYYMMDDHHMMSS).
 - Meta-data: Description of chamber system and analyser, results of system quality tests, picture of the ground covered with the chamber and the chamber location (JPG).

Non-linearity of fluxes

There are various schemes suggested for flux calculations which differ in their theoretical basis, numerical requirements and potentially, their accuracy and precision (Appendix: Table A1). From theory it is known that GHG fluxes in closed chambers are not constant during a chamber closure (Hutchinson and Mosier, 1981), resulting in non-linear concentration development within the chamber headspace. This non-linearity depends on chamber volume to the area ratio, the closure time, and it is also affected by incidental leakages of chamber or horizontal gas flow within the soil (e.g. Kutzbach *et al.*, 2007). The non-linearity of the fluxes can be accounted for adopting non-linear flux calculation methods which estimate the flux rate at the start of the chamber closure. On the other hand, the non-linear fitting is very sensitive to outliers in the measured GHG concentrations, and in some cases it can result overestimation of calculated GHG fluxes. Non-linearity can also be avoided by keeping the chamber closure time as short as possible.

Chamber closure duration is an important part of the chamber measurements. The closure duration should be as short as possible but long enough to reliably quantify the changes in all investigated GHGs. It should be based on the rate of concentration change of the investigated GHGs and precision of the used analyser. If the measurement duration is sufficiently short, the concentration change over the chamber closure follows a linear trend and hence the fluxes can be approximated by a linear model. The definition of a “sufficiently short” closure duration depends on the magnitude of the flux, chamber volume to the area ratio, air diffusivity of the soil and the type and precision of the gas analyser. Generally, five minutes is a sufficient time to obtain a reliable change in concentration of the investigated GHGs. On the other hand, in case of high fluxes, five minutes may already be too long and lead to non-linear concentration development (Appendix, Fig. A7). In this case, only a part of acquired data should be used for flux calculation.

A simple linear regression is adopted for flux calculation of any GHG at all the stations in order to use a standard and robust calculation method which allows measurements at different sites to be comparable. We acknowledge that in some cases and sites, this may lead to small underestimations of the fluxes due to non-linearity of the concentration change (e.g. Pihlatie *et al.*, 2013), as explained above. However, in order to have a general and robust flux calculation suitable for all sites, this is the current recommendation. As the raw data from all chamber measurements are saved in the data depository, it is possible to later adopt non-linear flux calculation methods, or site-specific flux calculations by the PI.

From experiences with measurements using infrared CO₂ analysers (soil CO₂ efflux) or laser absorption spectrometers N₂O/CH₄ analysers, it is known that measurements

shorter than about 5 min can be generally evaluated with a linear model. The first 10 to 20 s after closing the chamber (need to be determined from the raw data for each site setup individually) should be rejected due to incidental pressure variations in the chambers. The data thereafter can be used for flux calculation. The first value of GHG concentration for the flux calculation should be as close as possible to the moment of the chamber closure and must be a part of the linear trend of concentration increase. The possible maximum quantity of the values with near-linear trend should be used for flux calculation. The last acceptable measurement of concentration should be taken from the intersection of linear and exponential fitting curve (Appendix Fig. A7). It means that a “moving window” for the data selection will be applied.

In manual chamber measurements, it is recommended to use both linear and non-linear regression for flux calculation (Pihlatie *et al.*, 2013). If both result in the same flux rates, soil GHG concentration change over time follows a linear increase. If the methods differ, this could be either result from a real non-linear concentration development, but also from measurement errors. To clarify this, the concentration measurements need to be quality controlled by the PI, and based on this check decided by PI if non-linear or linear functions are applied.

RESULTS AND DISCUSSION

The chamber method for measuring GHG fluxes can be used with success in a wide variety of ecosystems (forest, grassland, cropland, wetland, *etc.*) depending on the individual needs of the measuring site. Generally, chamber methods are relatively low in cost and simple to operate. In combination with appropriate sample allocations, chamber methods are adaptable for a wide variety of studies from local to global spatial scales, and they are particularly well suited for *in situ* and laboratory-based studies (Livingston and Hutchinson, 1995). Different chamber techniques, including static and dynamic chambers (Yim *et al.*, 2003; Pumpanen *et al.*, 2004; Heinemeyer and McNamara, 2011; Pihlatie *et al.*, 2013; Wang *et al.*, 2013), have been used with varying degrees of success in estimating GHGs (CO₂, CH₄, N₂O) efflux. However, all of them have disadvantages which have either prevented them from giving an adequate estimation of GHGs emission or restricted them to use under limited conditions (Fang and Moncrieff, 1996). GHG exchange between soil and atmosphere is a complex process, therefore measurements by chamber systems are subject to many potential source of disturbances/errors. They could be grouped into: i) physical and biological disturbance related to the measurement processes, ii) errors associated with improper chamber design and with the sampling handling, and finally iii) errors related to sample analysis and inappropriate methods for computing fluxes (Livingston and Hutchinson, 1995). Despite the fast

development of other methods for quantifying GHGs (mainly CO₂ and CH₄) fluxes like EC, Relaxed Eddy Accumulation (REA) or Gradient Method (GM), chamber systems are still widely used. The use of EC or REA for soil CO₂ efflux measurement is too complicated or even impossible if the soil is covered by vegetation, because the methods are not able to separate fluxes from soil surface and above ground vegetation and even unable to directly reveal small-scale heterogeneity. The GM has been readily adopted due to the development of new low-cost and low-power CO₂ sensors. However, despite their widespread use, the utility of the GM is hindered by uncertainties associated with the application of *ex situ* published models of the soil diffusion coefficient, which is the only modelled parameter in the gradient method, yet its estimation is highly uncertain (Sánchez-Cañete *et al.*, 2016).

Bias and errors of chamber systems can be mostly overcome by using appropriate chamber design, relatively short sampling time and care to minimize site disturbances. Davidson *et al.* (2002) pointed out that chamber methods that are properly designed and deployed can provide a reliable means of accurately measuring soil CO₂ efflux in terrestrial ecosystems. Moreover, chamber methods are easily applicable to determine the soil GHGs efflux spatial heterogeneity, which is documented by the majority of chamber studies. Manual chamber measurements are usually made by one person who moves from location to location, therefore, such measurements cannot be provided frequently due to the time constraints of the manual operators (Savage and Davidson, 2003). Even though manual chamber measurements allow users to investigate the inter-annual variations of soil GHGs efflux and the influence of environmental factors during the growing season, they may not be consistent throughout the year and may miss specific weather events; such as rain, drought or heatwaves conditions. For example, the response of soil CO₂ efflux to precipitation events can be rapid and often missed due to the infrequency of manual measurements. Automated chambers have the great advantage of being able to measure continuously for long periods, regardless of the weather and time of day. The use of appropriated automated systems for soil GHGs efflux allows accurate measurements, minimal disturbance of the soil surface (minimize the operators walking on the measured area in comparison with manual measurement), and high resolution datasets for extended periods of time. However, automated systems can be more difficult to maintain, they generally require higher initial investment, a permanent energy supply is necessary for their continuous operation, and the number of measurement positions is limited. However, accurate measurements of GHG fluxes are extraordinarily challenging due to the complexity of GHG production, consumption and transport in a porous medium of soil. First, the GHG concentration in soil is usually many times greater than that in ambient air with a steep gradient. Second, the GHG transport from

deep soil layers to the surface is driven primarily by diffusion along these gradients. To cope with the challenges in measuring GHG fluxes, scientists have conducted extensive research the past several decades to develop a variety of measurement methods. Most commonly used approach is the chamber method, which provides direct measurements of GHG efflux from the soil surface.

Since the CO₂, CH₄ and N₂O measurements shall be conducted continuously and long-term, the automated chamber system was chosen as the most appropriated technique. Automated chamber systems, which are properly developed and deployed, allow obtaining accurate GHG measurements at a high temporal resolution dataset and for extended periods of time. Manual chamber can be used complementary.

CONCLUSIONS

1. Profound understanding of the driving forces of climate change and evaluation of the mitigation activities requires long-term and high precision measurements of greenhouse gas emissions and sinks and their evolution.
2. Standardised measurements of greenhouse gases and flux calculation increase the access and usability of data. It will also improve the inter-comparability between ecosystem stations and years.
3. Automated chamber systems working in closed dynamic mode will be applied as a standard method for greenhouse gases flux measurements in ICOS stations and as a supporting method for eddy covariance technique.
4. Harmonisation of the chamber method facilitates applicability of this method to various terrestrial ecosystems at different greenhouse gases monitoring networks.
5. Disturbance of vegetation excluding (*e.g.* clipping, removing) is not allowed for automated chamber measurements of soil CO₂ efflux.
6. Measurements of net ecosystem exchange (NEE) by transparent chambers are not foreseen within ICOS since NEE is already determined by EC towers at ICOS station. Therefore, transparent chambers and the respective issues are not in the focus of this manuscript. Notwithstanding, we recommend the use of transparent chamber in order to quantify the contribution of ground vegetation to the NEE in stations where the contribution of ground vegetation is relevant.

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Appendix

The inaccuracy of the calculation of CO₂ efflux can be caused by measurement errors in several parameters: chamber volume, chamber surface area, air pressure, air temperature and analyser accuracy. We created models, which demonstrate the error (%) in efflux calculation when one parameter is entered with an error while the others are entered 100% correctly. The models were demonstrated on a cylindrical chamber with volume of 0.00107 m³, covering area of 0.0084 m², under air temperature of 15 °C and air pressure 99800 Pa. For the efflux calculation the linear fitting was used.

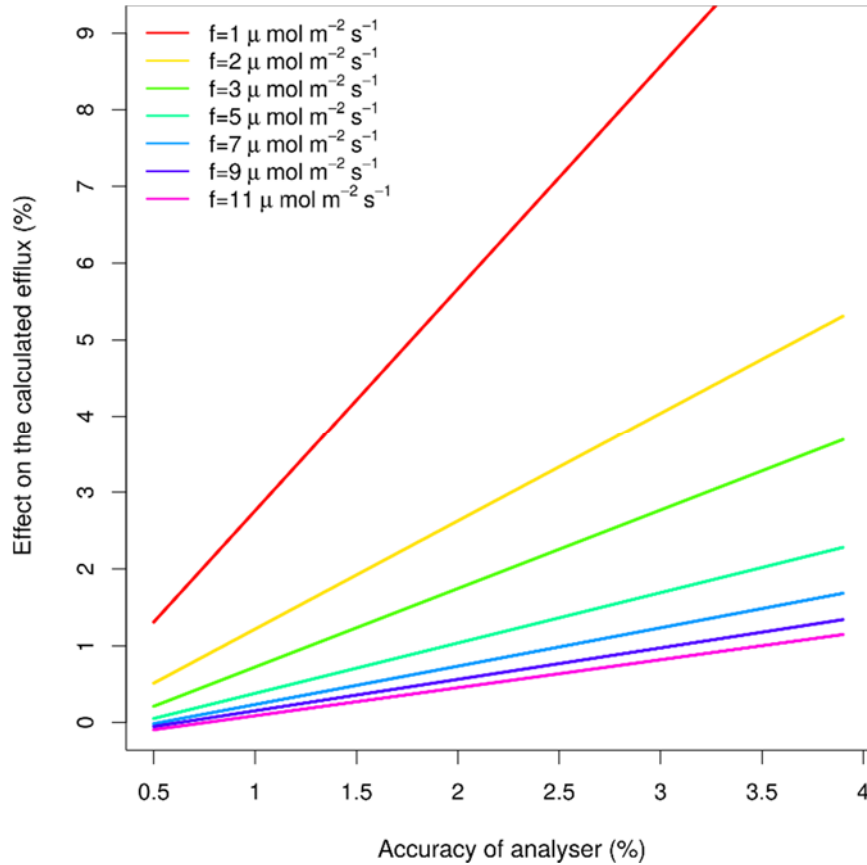


Fig. A1. The error of calculated efflux increased linearly with increasing error of the analyser for all tested efflux rates. The commonly used analyser type LI-COR 840(A) has the accuracy 1 %. It can result in the error in efflux calculation up to 0.2–2.7 % depending on measured efflux rates.

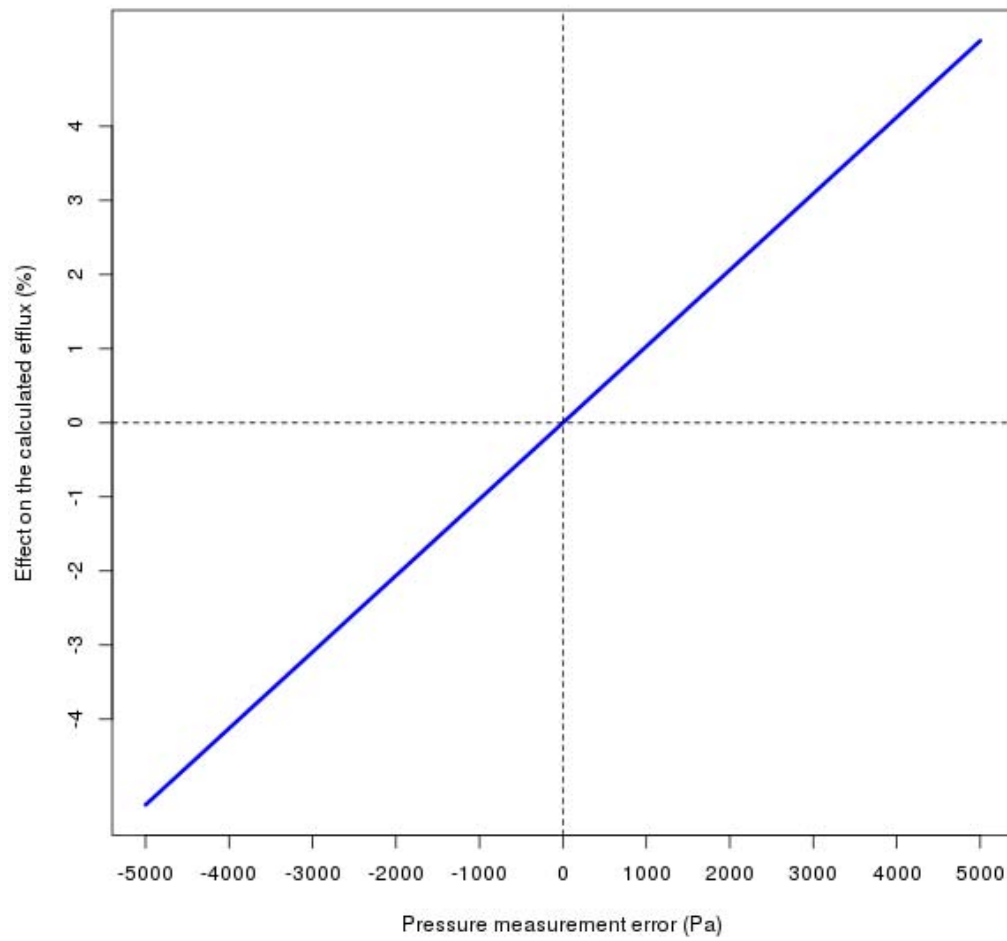


Fig. A2. The error of calculated efflux increased linearly with increasing error of measured air pressure. The error of 1000 Pa results in the 1% error in the efflux calculation. The air pressure sensors usually range below this value, therefore we can consider that continuous measurements of air pressure will not cause high inaccuracy of efflux calculation. The problem can develop when one value of air pressure is set for the whole measurement period.

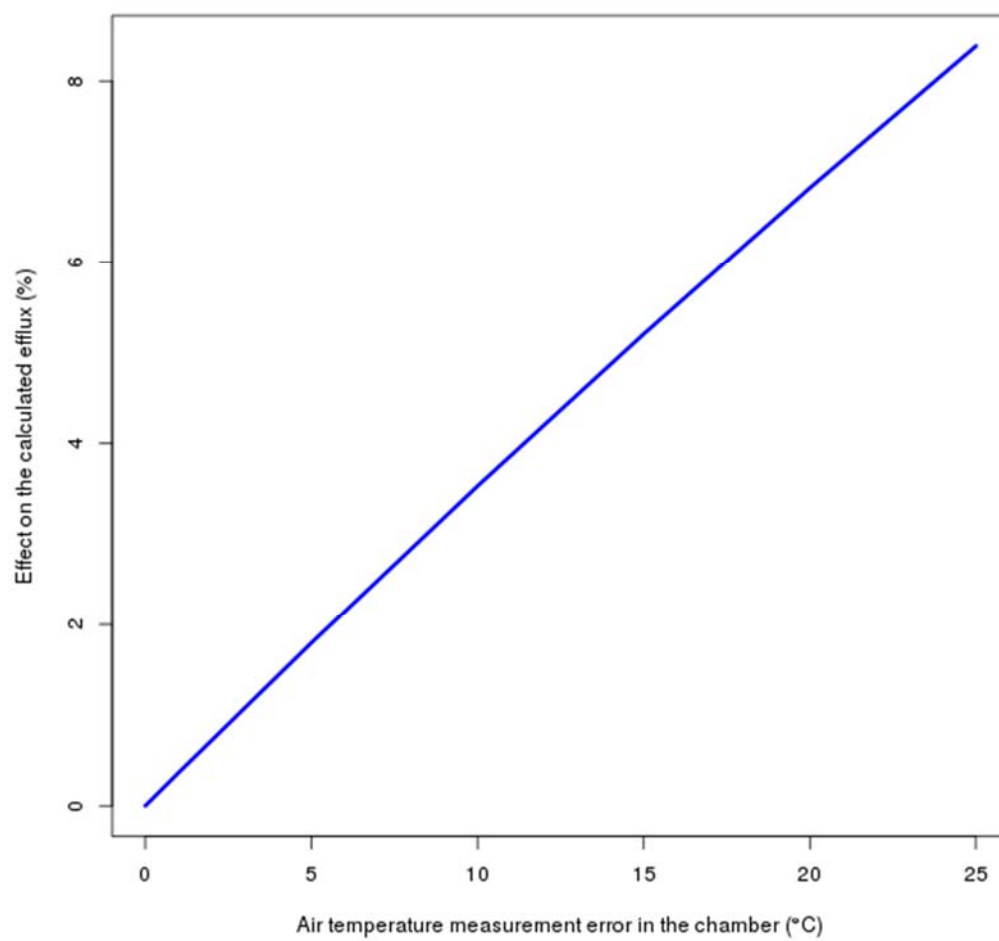


Fig. A3. The error of calculated efflux increased linearly with increasing error of measured air temperature. The 1% error of calculated efflux would be caused by the air temperature inaccuracy of 3 °C.

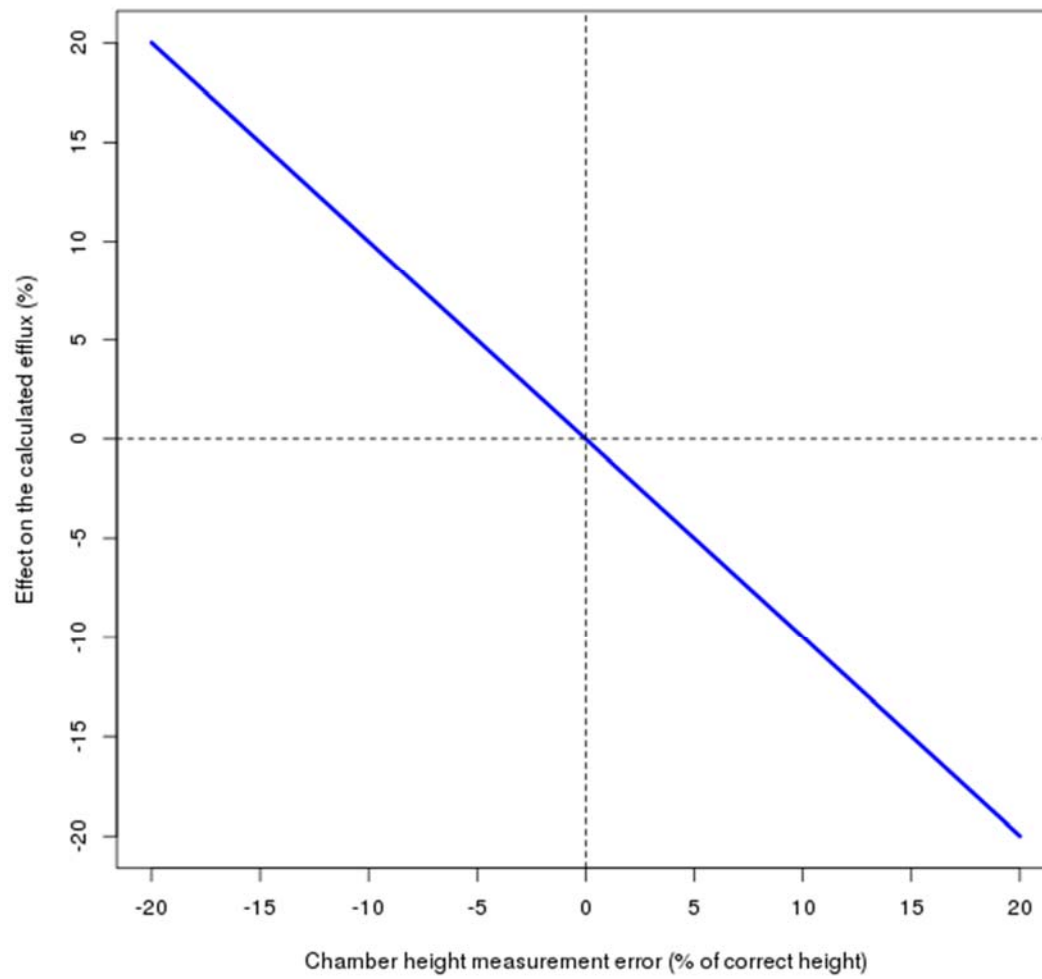


Fig. A4. There is linear relationship between error of calculated efflux and error of chamber height. The possible inaccuracy (%) of the chamber height measurement can increase in small chambers. However, it should not exceed 5%, which causes also 5% error in calculated efflux.

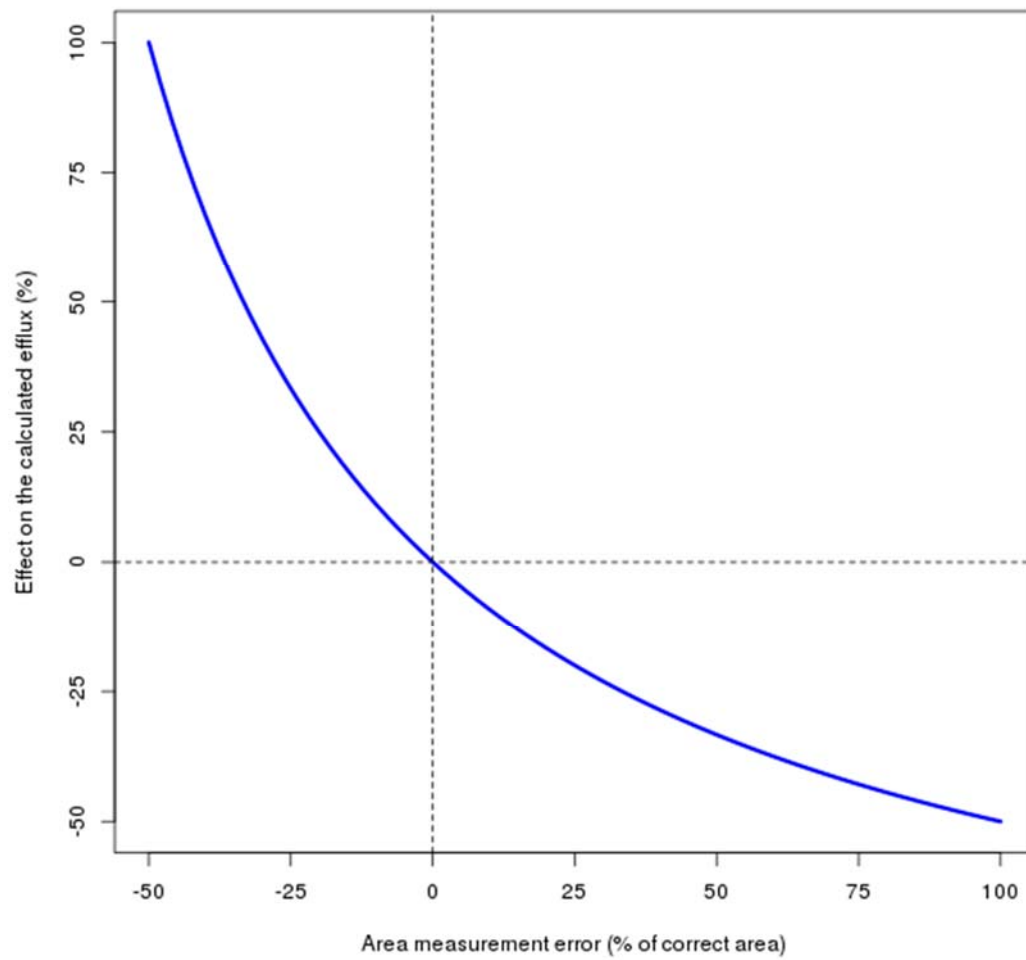


Fig. A5. The error of calculated efflux is hyperbolically addicted of area measurement error. The efflux calculation error of 5% can be caused already when the error of the area is 5%. Therefore, the surface area should be measured carefully in the small chambers.

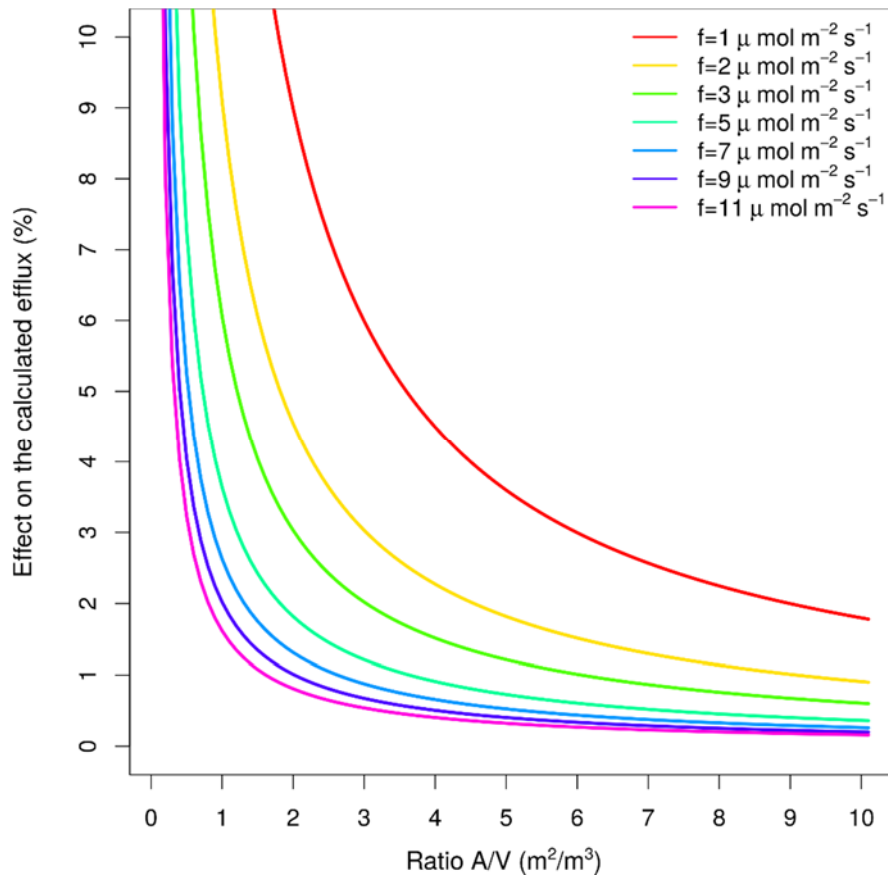


Fig. A6. The shape of chamber (area/volume ratio) has effect on efflux calculation accuracy. The error decreases with the ratio in hyperbolic shape. For the efflux rates of 5-11 $\mu\text{mol m}^{-2} \text{s}^{-1}$ the error starts to increase sharply at the ratio about 1.5. For the lower efflux rates the sharp increase starts at higher ratios (2.5 – 5).

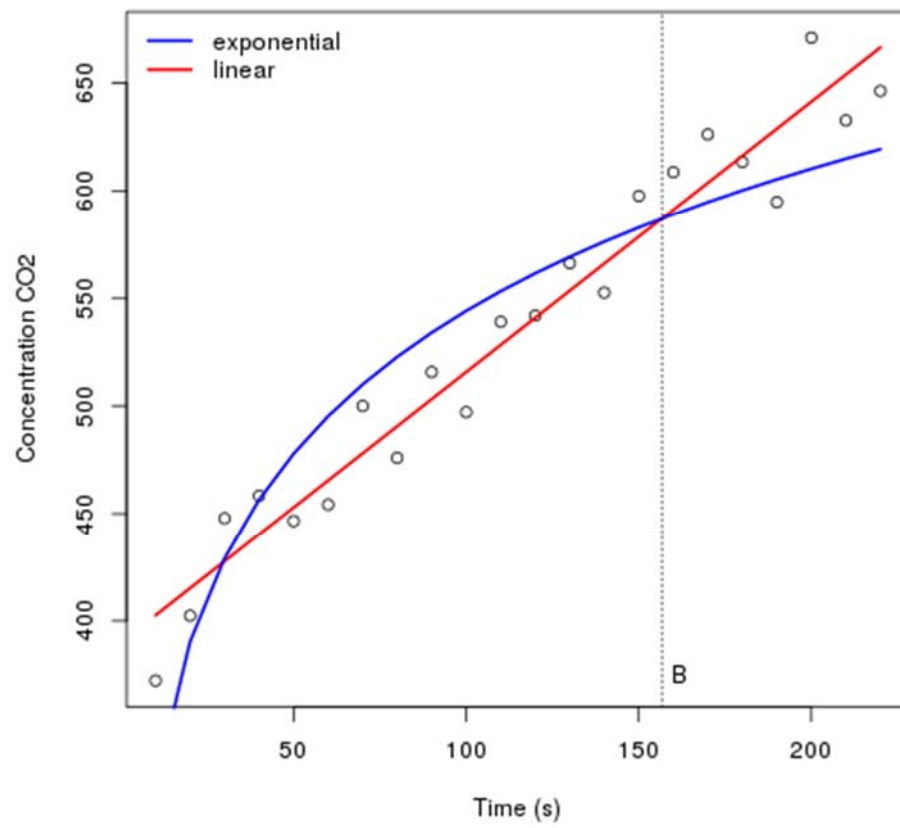


Fig. A7. This procedure was used to determinate the point B – the time where flux lost its linearity. At first, the data is sorted by time. Then, they are extrapolated by two curves – regression line p (red line) and exponential curve K (blue line). The intersection of p and K is point B.

Table A1: Summary of key advantages, disadvantages and recommendations for selection of flux calculation scheme according to De Klein and Harvey (2012).

Schema	Advantages	Disadvantages	Recommendations
Conventional FC schemes			
LR: (linear regression)	Least sensitive to measurement error (most precise) of all methods. Least-biased method for convex-upward curvature. Computationally simple.	Empirical, with no basis in diffusion-theory. Most biased method for convex-downward curvature.	Recommended option with: Three sampling points, or; > 3 sampling points, and convex-upward curvature is observed.
HM (Hutchinson and Mosier)	Based on quasi steady-state diffusion theory. Least-biased conventional scheme for convex-downward curvature.	Restricted to three equally-spaced time points. More sensitive to measurement error (less precise) than LR and QR.	Not recommended, because of high imprecision and availability of improved non-linear methods.
QR (Quadratic regression)	Not limited to three equally-spaced sampling points. More precise than HM method. Less biased than LR for convex-downward curvature.	Empirical, with no basis in diffusion theory More biased for convex-downward curvature than other non-linear methods.	Recommended option with: ≥ 4 sampling points.
Advanced Fc schemes			
NDFE (Non-steady state diffusion flux estimator)	Based on non-steady state, one-dimensional diffusion theory, with clearly defined physical assumptions. Provides ‘perfect’ calculation of flux at zero time, when all assumptions are held and with no measurement error.	Highly sensitive to violation of underlying assumptions. Can deliver more than one flux value for a given data set and/or unexpectedly high flux values. Not easily adapted to spreadsheets, nor efficient for handling large data sets.	Recommended option with: ≥ 4 sampling points.
HMR	Based on the same theory as HM method, but with	More sensitive to random measurement error (less	Recommended option with:

(HMR method)	<p>additional consideration of lateral (two-dimensional) gas transport beneath chambers.</p> <p>Available as part of software package that provides confidence intervals for estimated flux values.</p>	precise) than LR and QR, especially at lower flux values.	>4 sampling points.
CBS (Chamber bias correction method)	<p>Same theoretical basis as NDFE method.</p> <p>Delivers a single flux value, avoids unexpectedly high flux values given by NDFE and less sensitive to violation of assumptions than NDFE.</p> <p>Can be combined with QR or LE methods.</p>	<p>Requires additional soil data, which may introduce error.</p> <p>Requires multiple calculations (but can be done in spreadsheet format).</p>	<p>Recommended option when accurate soil bulk density and water content data are available, with ≥ 3 sampling points when combined with LR or, ≥ 4 sampling points. combined with LR or QR.</p>

Table A2: Literature overview on published protocols and recommendations for soil-atmosphere GHG measurements with emphasis on the static chamber methodology according to Butterbach-Bahl *et al.* (2016). Publications with star are core publications to the specific topic

Topic	Methods	Highlights	References
General overviews on methodology			
CH ₄ and N ₂ O fluxes flux measurements	Overview on techniques	Very useful theoretical and practical information on distinct measurements	Denmead (2008)
Measurement methods of CH ₄ fluxes in rice paddies/ wetlands/uplands	Overview about micrometeorological and chamber techniques	Overview on measuring techniques	Schütz and Seiler (1992)
CH ₄ and N ₂ O fluxes from livestock systems	Overview on techniques	Review of the approaches and underlying mechanisms/ processes	Kebreab <i>et al.</i> (2006)
Measurement methods of soil GHG fluxes	Overview on techniques with focus on static chamber measurements	Overview on methodologies and short-comes	Butterbach-Bahl <i>et al.</i> (2011)
Quality assurance for static chamber measurements	Static chamber measurements	Minimum set of criteria for static chamber design and deployment methodology, confidence in the absolute flux values reported in about 60% of the studies was estimated to be very low due to poor methodologies or incomplete reporting	Rochette and Eriksen-Hamel (2008)*
Micrometeorological measurements of N ₂ O, CO ₂ , CH ₄	Description of measurement procedures	Summarising theory and application of micrometeorological measurements of GHG fluxes from soils	Pattey <i>et al.</i> (2006); Aubinet <i>et al.</i> (2012); Eugster and Merbold (2015)
Chamber measurement protocols			
Soil N ₂ O flux measurements	Static chamber measurements	Detailed step by step description of procedures	De Klein and Harvey (2012)
Measurements of N ₂ O and CH ₄ fluxes from agricultural sources	Overview about micrometeorological and chamber techniques, incl. techniques to measure CH ₄ emissions from ruminants	Standard text book on method to measure agricultural GHG fluxes for reference	IAEA (1992)
Chamber measurements of N ₂ O, CH ₄ , CO ₂ fluxes	Chamber measurements	Overview on calculations and practical recommendations for chamber measurements; standard protocol for the USDA-ARS GRACEnet project	Parkin and Venterea (2010)

Sampling times and dates for CH ₄ flux measurements in rice paddies	Chamber measurements	Simplified measuring protocol for CH ₄ fluxes from rice paddies to minimize number of measurements	Buendia <i>et al.</i> (1998)
Soil N ₂ O flux measurements	Static chamber measurements	Discusses potential errors when installing static chambers and provides minimum requirements for using these chambers	Rochette (2011)
Common practices for manual GHG sampling	Static closed chamber measurements	Literature review of the most widely used methodological features of manual GHG sampling identified	Sander <i>et al.</i> (2014b)
Flux calculation for static chamber technique			
Non-linear versus linear calculation methods for soil N ₂ O fluxes	Static chamber measurements	Linear calculation schemes are likely more robust to relative differences in fluxes	Venterea <i>et al.</i> (2009)
Diffusion model	Static chamber measurements	Common measurement practices and flux calculations underestimate emission rates by 15-25% under most circumstances; error dependent on chamber height, soil air porosity and flux calculation method	Livingston <i>et al.</i> (2005)*
Flux correction for static chamber measurements of N ₂ O and CO ₂ fluxes	Static chamber measurements	Correction scheme for estimating the magnitude of flux underestimation arising from chamber deployment	Venterea <i>et al.</i> (2010)
Flux correction	Static chamber measurements	The systematic error due to linear regression is of the same order as the estimated uncertainty due to temporal variation	Kroon <i>et al.</i> (2008)
Flux correction	Static chamber measurements	Linear versus non-linear; provides link to free R software download for flux calculation	Pedersen <i>et al.</i> (2010)*
Flux correction	Static chamber measurements	Significant underestimation of soil CO ₂ flux strength if linear regression is applied	Kutzbach <i>et al.</i> (2007)
Theoretical evaluation	Static chamber measurements	Measurement and simulation of measuring errors	Hutchinson and Rochette (2003)
Theoretical evaluation	Static chamber measurements	Review and suitability of several calculation procedures	De Klein and Harvey (2012)
Headspace N ₂ O increase	Static chamber measurements	Increased headspace concentration of N ₂ O reduced effective efflux of N ₂ O from the soil	Conen and Smith (2000)
Chamber design and comparison of methods			
Comparison of chamber designs and linear versus non-	Static chamber design intercomparison	Increasing chamber height, area and volume significantly reduces flux underestimation	Pihlatie <i>et al.</i> (2013)

linear flux calculation			
Chamber measurements of soil N ₂ O fluxes	Closed and dynamic chamber measurements	Comparison of different chamber types (sizes) with EC fluxes	Smith <i>et al.</i> (1996)
Static chamber and vent design, flux calculation method for soil N ₂ O flux estimates	Static chamber measurements	Vent dimension affects N ₂ O fluxes, one of the first papers on chamber design, flux calculations and venting	Hutchinson and Mosier (1981)
Venting of static chambers			
Effect of venting on N ₂ O flux measurements	Comparison of vented versus non-vented closed chambers	Venting can create larger errors than the ones it is supposed to overcome	Conen and Smith (1998)
Effect of venting on CO ₂ flux measurements on forest soils	Comparison of vented versus non-vented closed chambers	Increases of CO ₂ fluxes exceeding a factor of 2 in response to wind events for vented chambers	Bain <i>et al.</i> (2005)
Vent design	Closed chambers	Presenting a new vent design to avoid overestimation of CO ₂ fluxes under windy conditions due to the Venturi effect	Xu <i>et al.</i> (2006)
Vent design and seals	Closed chambers	Discussion on the necessity of vents and appropriate flux calculation	Hutchinson and Livingston (2001)
Chambers and small scale variability of fluxes			
Effect of soil physical characteristics on fluxes	Chambers	Re-iterates effects of non-steady soil conditions (small-scale heterogeneity) on errors while measuring fluxes with chambers	Venterea and Baker (2008)
Sampling frequency and number of chambers for overcoming spatial heterogeneity of soil CO ₂ fluxes	Static chambers	Means of eight randomly chosen flux measurements from a population of 36 measurements made with 300 cm ² diameter chamber were within 25% of full population mean 98% of the time and were within 10% of the full population mean 70% of the time	Davidson <i>et al.</i> (2002)
Overcoming spatial heterogeneity with a gas pooling technique	Static chambers	Pooling of gas samples across individual chambers is an acceptable approach to integrate spatial heterogeneity	Arias-Navarro <i>et al.</i> (2013)
Timing of measurements, sampling frequency and cumulative fluxes			
Evaluation of the importance of sampling time for N ₂ O flux estimates	Comparison of auto-chambers with replicated manual chambers	Auto-chambers are useful if significant diurnal fluctuations in temperature are expected and for better quantifying fertilization emission pulses	Smith and Dobbie (2001)

Effect of sampling frequency on cumulative N ₂ O fluxes estimates	Automated measuring system	Sampling once every 21d yielded estimates within -40% to +60% of the actual cumulative flux	Parkin (2008)
Evaluation of effects of sampling frequency on N ₂ O flux estimates	Automated measuring system	Low frequency measurements might lead to annual estimates which differ widely from continuous, automated flux measurements (e.g. 1 week = -5 - +20%)	Liu <i>et al.</i> (2010)
Evaluation of best daily sampling time for N ₂ O flux estimates	High frequency manual measurements	21:00-22:00 h and 09:00-10:00 h were the times that the flux best represented the daily mean	Alves <i>et al.</i> (2012)
Chamber effects on soil environmental conditions	Static chamber measurements, comparison of automated and manual chambers	Seasonal cumulative N ₂ O and CH ₄ fluxes as measured by manual chambers on daily basis were overestimated 18% and 31%, since diurnal variation in fluxes were not accounted for; on the other side, automated chambers reduced soil moisture; to avoid this, change of chamber positions is recommended	Yao <i>et al.</i> (2009)
Effects of sampling frequency on carbon loss estimation	Automated measuring system	As sampling interval increased from 1 d to 12 d, the variance associated with cumulative flux estimates increased; sampling once every 3 d, estimates of cumulative C loss were within 20% of the expected value	Parkin and Kaspar (2004)
Sampling frequency, systematic sampling uncertainty and measurement errors of soil respiration	Automated measuring system	A weekly or bi-weekly manual sampling strategy is likely sufficient if the desired outcome is an annual estimate of CO ₂ efflux; if modelling SR on time scales from minutes to days is the purpose of the study, automated SR measurements are advantageous	Savage <i>et al.</i> (2008, 2014)
Sampling frequency and diurnal pattern of soil CO ₂ efflux/ respiration	Automated measuring system	The smallest difference between modelled and continuously measured CO ₂ efflux was observed at 20:00 and the highest at 04:00	Darenova <i>et al.</i> (2014)
CH ₄ and N ₂ O fluxes from manure slurry storage system	Comparison of continuous and non-continuous flux measurements	Recommendations of sampling intervals and timing of measurements; for CH ₄ , sampling between 18:00 and 08:00h at intervals <7d yielded ±10% deviation for N ₂ O was 50% when sampling at 20:00h	Wood <i>et al.</i> (2013)
Winter flux measurements in snowy conditions			
Introducing the snowpack concentration gradient method	Snowpack concentration gradient method	First description of the method; includes method specific accuracy and precision estimates for each gas	Sommerfelt <i>et al.</i> (1993)

CO ₂ , CH ₄ and N ₂ O fluxes from alpine forest soil	Static chamber measurements	Practical description on measuring the flux with direct insertion of the chamber through snowpack	Groffman <i>et al.</i> (2006)
CO ₂ fluxes from sub-alpine forest	Snowpack concentration gradient method	Introduces an automated sample collection system; discusses limitations of the method and presents error estimations for snow density measurements	Seok <i>et al.</i> (2009)
CO ₂ fluxes from the arctic	Comparison of floating chambers and snowpack concentration gradient method	Includes a review on winter flux measurements at various arctic ecosystems; introduces using SF ₆ as tracer for improved diffusion estimates, reports that different methods result flux estimates differing by two orders of magnitude	Björkman <i>et al.</i> (2010)
CO ₂ fluxes from sub-alpine forest	Snowpack concentration gradient method	Includes a useful review comparing winter fluxes from different ecosystems	Liptzin <i>et al.</i> (2009)
CO ₂ , CH ₄ and N ₂ O fluxes from sub-alpine grassland	Snowpack concentration gradient method	Describes sampling for all three gases, introduces using ²²² Rn for improved diffusion estimates	Merbold <i>et al.</i> (2013)
CO ₂ fluxes from forested peatland	Dynamic automatic chamber measurements	Includes a description of chamber system which can be adjusted for different snow pack thicknesses	Koskinen <i>et al.</i> (2014)
